

Total arsenic, cadmium, lead, mercury and tin, and extractable cadmium and lead in feed of plant origin

Interlaboratory Comparison Report

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IMEP-29: Total arsenic, cadmium, lead, mercury and tin, and extractable cadmium and lead in feed of plant origin

Interlaboratory Comparison Report

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1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme® IMEP. It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of total As, Cd, Pb, Hg and Sn, and extractable Cd and Pb in feed of plant origin following Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed [1].

The test material used in this exercise was a candidate reference material, the matrix being rye grass. The material was relabelled and dispatched to the participants in the second half of October 2009. Each participant received one bottle containing approximately 10 g of test material. Sixty-two participants from 23 countries registered to the exercise of which 59 reported results.

The assigned values (X_{ref}) for total Cd, Pb, As, Hg and Sn were the reference values as obtained during the certification campaign taking place simultaneously to the ILC. The assigned values for extractable Cd and Pb were provided by IRMM using isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS).

Participants were invited to report the uncertainty of their measurements, which was done by around 90 % of them. The laboratory performance was evaluated using z- and ζ -scores in accordance with ISO 13528 [2]. The standard deviation for proficiency assessment (also called target standard deviation), $\hat{\sigma}$, was fixed at 15 % for all measurands on the basis on the outcome of previous ILCs.

The outcome of the exercise was altogether positive, with 68 % or more of the participants reaching satisfactory z-scores for all measurands except for total As and Hg, which appeared to be problematic in this exercise, showing a non-normal results distribution and tendency to very high means. The ζ -scores were not as good as the z-scores, which indicates a persisting problem of appropriate uncertainty estimation. Finally, total Sn was included for the first time in an ILC. Results were better than expected, but can certainly be improved.

2 IMEP support to EU policy

The International Measurement Evaluation Programme® (IMEP) is owned by the JRC - IRMM. IMEP provides support to the European measurement infrastructure in the following ways:

IMEP **distributes metrology** from the highest level down to the field laboratories. These laboratories can benchmark their measurement result against the IMEP reference value. This value is established according to metrological best practice.

IMEP helps laboratories to assess their estimate of **measurement uncertainty**. The participants are invited to report the uncertainty on their measurement result. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising intercomparisons in the frame of specific EU Directives, or on request of a specific Directorate-General. IMEP-29 provided specific support to the following stakeholders:

- To the European Co-operation for Accreditation (EA) in the frame of a formal collaboration on a number of metrological issues, including the organisation of intercomparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-29. Mr. Ian Mann from the Swiss Accreditation Service (SAS) liaised between EA and IMEP for this intercomparison. This report does not discern the EA nominees from the other participants. Their results are however summarised in a separate report to EA.
- To the Asia Pacific Laboratory Accreditation Cooperation (APLAC), in the frame of the collaboration with EA. The chair of the APLAC Proficiency Testing Committee, Mr. Dan Tholen, was invited to nominate a limited number of laboratories for this first collaboration.
- To the Community Reference Laboratory for Heavy Metals in Feed and Food (CRL-HM) in the frame of the support to the National Reference Laboratories (NRLs). The exercise was announced to the network of NRLs and they were invited to distribute the information between routine laboratories in their country. The results gathered in IMEP-29 represent the state of the art of the official control laboratories involved in analysis of feed in Europe.

3 Introduction

Metals occur in varying amounts as natural ingredients of the earth's crust and thus can also be determined in variable concentrations in plants and animals, and consequently also in food and feed. Concerning food and feed of plant origin, the genetic properties of the plants, the nature of the soil on which the plants are grown, the climate and the degree of maturity of the plant at the time of harvesting have a considerable influence on the content of elements in the plant. Apart from genetics, the nature of the soil is one of the most important factors. Depending on the existing geological conditions of the particular region, the element content of the soil can vary by several degrees of magnitude. The

concentration of elements in plants is largely correlated to the corresponding concentrations in the soil on which they grow, though differences in the acid content, the humus layer, and the structure of the soil itself will also have some influence. The heavy metal content of the soil can be detrimentally affected by anthropogenic activities, such as the use of contaminated mineral fertilisers, or spreading sewage sludge contaminated with heavy metals or sediments dredged from polluted rivers. In certain polluted areas the heavy metal content can reach levels several times higher than normal, so that the plants grown there can be used neither as feed nor food according to the applicable legislation [3].

To overcome problems associated with a high metal content in feed, maximum levels for trace elements in several commodities have been laid down in Directive 2002/32/EC [1], and a network has been built up to ensure quality and comparability in official controls throughout the European Union. In March 2006 a footnote was introduced in Directive 2002/32/EC in which it is stated that "*Maximum levels refer to an analytical determination of lead and cadmium whereby extraction is performed in nitric acid 5 % (w/w) for 30 min at boiling temperature*".

In support to the Directive 2002/32/EC, IMEP organised a proficiency test (PT) on heavy metals in feed. This exercise was carried out in parallel with the CRL-HM / IMEP-108. The same test material was used in both exercises. IMEP-29 was open to all laboratories involved in this type of analysis.

4 Scope

The scope of this ILC is to test the competence of the participating laboratories to determine the total mass fraction of As, Cd, Pb, Hg and Sn, and the extractable mass fraction of Cd and Pb in feed of plant origin. The assessment of the measurement results is undertaken on the basis of requirements laid down in EU legislation [1] and follows the administrative and logistics procedures of IMEP (IRMM). This programme is accredited according to ISO Guide 43-1.

5 Time frame

The interlaboratory comparison was agreed upon by the NRL network at the third CRL-HM workshop held on 25-26 September 2008. Specific details of the exercise were refined during the fourth CRL-HM workshop held on 1-2 October 2009. The ILC was announced to the various stakeholders between 14 and 22 October 2009. IMEP-29 was made public on the IMEP webpage [4] on 22 October 2009.

Interested laboratories could register until 15 November 2009. Samples were sent out to the laboratories on 18 – 19 November 2009. For all laboratories the deadline for reporting results was the 3 January 2010.

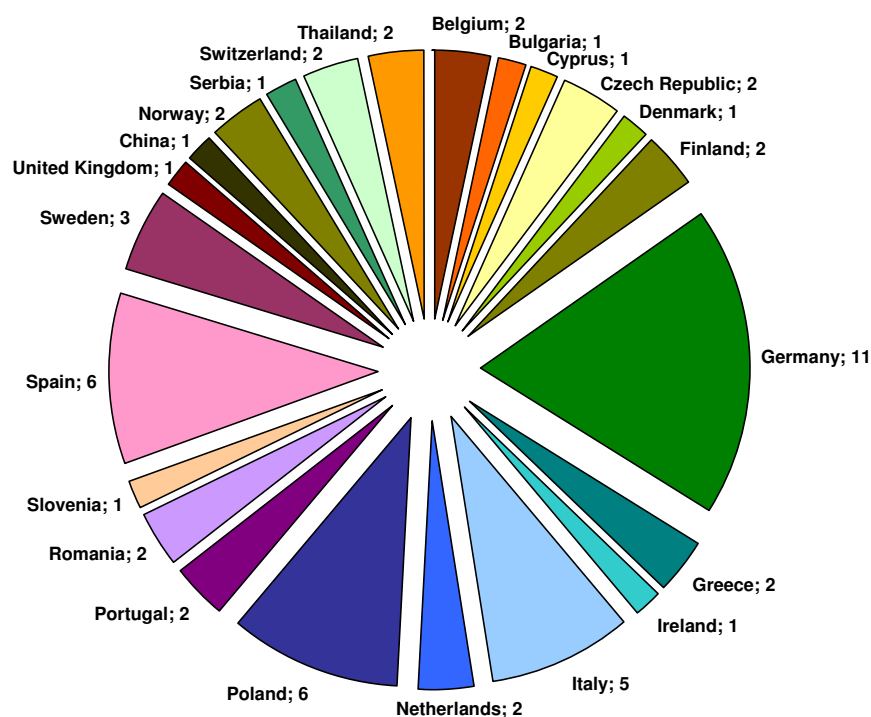
6 Invitation, registration and distribution

Invitations for participation were sent to the EA coordinator (Annex 1) and APLAC responsible (Annex 2) for distribution to nominated and interested laboratories. NRLs involved in IMEP-108 were informed via email (Annex 3) about this parallel exercise to give them the opportunity to invite laboratories from their respective countries. The web announcement on the IRMM website can be found in Annex 4.

Instructions on measurands, sample storage, reconstitution and measurement were sent to the participants together with the samples. The letter also contained the individual code for access to the result reporting website and further details on the envisaged time frame (Annex 5).

The participants who had submitted a result received the reference value four weeks after the reporting interface was closed. Fig 1 shows the participating countries and the number of participants having reported results.

Fig 1- Country distribution in IMEP-29 based on number of participants having submitted results



6.1 Confidentiality

EA was invited to nominate laboratories for participation. The following confidentiality statement was made to EA: "Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA

working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure."

6.2 Distribution

The ILC sample was dispatched by IRMM on 18 – 19 November 2009 to the participants. Each participant received one bottle containing approximately 10 g of test material, an accompanying letter with instructions on sample handling and reporting (Annex 5) and a form that had to be sent after receipt of the test material to confirm its arrival (Annex 6).

The dispatch was followed by the messenger's parcel tracking system on internet and in most of the cases the sample was delivered within a couple of days. In two cases, the dispatch took longer than the one-week period. It was however assumed that the parcel was not submitted to high enough temperatures or long enough time to have an impact on the samples' stability.

6.3 Procedure to apply

Concrete instructions were given to all participants in a letter that accompanied the test material. The measurands and matrix were defined as "Total As, Cd, Pb, Hg and Sn, and extractable Cd and Pb in feed of plant origin". Laboratories were asked to perform two or three independent measurements and report them, together with the mean of the results and its associated uncertainty. The measurement results were to be corrected for water following a procedure described in the accompanying letter (Annex 5) and for recovery. Participants were asked to follow their routine procedures, except for the determination of extractable Cd and Pb, where a procedure was given in the same letter. The results were to be reported in the same manner (e.g. number of significant figures) as those normally reported to customers.

The results were to be reported in a special on-line form for which each participant received an individual access code. A special questionnaire was attached to this on-line form. The questionnaire was intended to provide further information on the measurements and the laboratories. A copy of the questionnaire is presented in Annex 7.

7 Test material

7.1 Preparation

The rye grass used for the test material has been harvested in 1983. The original material was processed by jet milling and made separated in 25 g portions. The finely ground powder form was

further processed by drying at 50 °C (to reach the water content below 4 % (w/w)), homogenising and filling into amber 60 mL glass vials with a lyo-insert and an aluminium cap under argon atmosphere. Capping and labelling was performed according to the filling sequence. Every unit contains about 10 g of the rye grass material.

The particle size distribution of the final product was assessed using a Sympatec Helos laser diffraction instrument (Clausthal-Zellerfeld, DE). The maximum particle size was 175 µm. A sieve analysis demonstrated presence of larger particles of 200 µm to 3 mm. In relation to the total number of particles, their relative abundance is far below 1 %.

7.2 Homogeneity and stability

Homogeneity and stability studies were not undertaken because they have been conducted in the frame of the certification project for the total content of heavy metals, and on the basis of previous experience of the CRL-HM, extractable Cd and Pb behave the same than total Cd and Pb, respectively, in terms of homogeneity and stability.

8 Reference values and their uncertainties

The assigned values (X_{ref}) for total Cd, Pb, As, Hg and Sn were the reference values as obtained during the certification campaign of the test material that took place in the same period of time as IMEP-29. The assigned values for extractable Cd and Pb were provided by IRMM using ID-ICP-MS (Table 1).

The uncertainty in the reference concentration values (u_{ref}) for the total content of Cd, Pb, As, Hg and Sn, is calculated according to the method described in ISO Guide 35 by the Reference Materials Unit of IRMM. For extractable Pb, the u_{ref} for total Pb was taken, because the total and the extractable amounts of Pb in the test material were found to be identical.

The analytical uncertainty of X_{ref} (u_{char}) for extractable Cd was calculated according to the Guide to the Expression of Uncertainty in Measurement [5]. The uncertainty of the assigned value for extractable Cd was estimated combining the analytical uncertainty (u_{char}) with a contribution for the between-bottle homogeneity (u_{bb}) as provided by the test material producer. No contribution for the short-term stability of the materials was added because the material proved to be stable for the five weeks that elapsed between the dispatch of the test material and the deadline for submission of results.

As summarised in Table 1, total digestion and partial extraction of the test material, following the procedure described in the accompanying letter to the participants, provide identical Pb concentrations.

In the case of Cd, the reference value obtained by IRMM for extractable Cd is about 94 % of the total concentration.

Table 1 - Assigned values and their associated expanded uncertainties for the measurands of this ILC.

Measurand	X_{ref} (mg kg ⁻¹)	U_{ref} (mg kg ⁻¹)
Total Cd	0.120	0.007
Extractable Cd	0.114	0.003
Total Pb	1.67	0.11
Extractable Pb	1.67	0.11
Total As	0.042	0.010
Total Hg	0.0164	0.0022
Total Sn	0.062	0.011

X_{ref} is the reference value and $U_{\text{ref}} = k \cdot u_{\text{ref}}$ is the estimated associated expanded uncertainty; with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 %.

9 Evaluation of results

9.1 General observations

From the 62 laboratories that registered for participation, 59 submitted their results and completed the associated questionnaire. Of the 59 participants, 56 gave results for total Cd and Pb, 51 for total Hg, 49 for total As, 38 for extractable Cd, 37 for extractable Pb and 27 for total Sn. From these results, those reporting "0" or "less than" values were not included in the evaluation. This was the case for 10 laboratories for total As, 9 for total Sn, 6 for total Hg and 2 laboratories for extractable and total Cd.

Participant 3102 submitted results into the online system, but did not send any confirmation. It should also be mentioned that participant 2849 and 9763 reported for total As, and participant 9611 for extractable Cd, a "less than" value which was lower than the corresponding $X_{\text{ref}} - U_{\text{ref}}$ value, which has to be considered as an incorrect statement since they should have detected the respective element.

Concerning the three non-submissions, one laboratory cancelled its participation because of its participation in the IMEP-108, and the other two did not provide us with any information or justification.

No obvious wrong result reporting was observed, except for participant 0529 whose first measurement value for total Cd (0.99) was about ten times higher than the other three (~0.1), which seemed being a typing mistake in the first value. In this case, the co-ordinator took the freedom to correct this by inserting a '0' after the dot.

9.2 Uncertainties and coverage factor

All except six participants reported an uncertainty associated to their results, which is a very satisfying observation (~ 90 %). Three participants reported uncertainties for only some of their results.

The laboratories were asked to perform 1 to 3 replicates, and to report them together with the mean, its associated uncertainty and the expansion factor. Six laboratories reported an uncertainty with each single replicate result. One out of the six reported different uncertainties with the measurements, but none with the result's mean, and so the mean uncertainty was taken for the results evaluation.

Concerning the factor k , of the 53 participants who submitted an uncertainty with their results 14 (~ 25 %) did not give a value for the coverage factor. One participant gave an unreasonable value for k (100). This situation can certainly still be improved.

9.3 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z - and ζ -scores in accordance with ISO 13528 [2] and the IUPAC International Harmonised Protocol [6].

$$z = \frac{X_{\text{lab}} - X_{\text{ref}}}{\hat{\sigma}} \quad \text{and} \quad \zeta = \frac{X_{\text{lab}} - X_{\text{ref}}}{\sqrt{u_{\text{ref}}^2 + u_{\text{lab}}^2}}$$

where:

- X_{lab} is the measurement result reported by a participant
- X_{ref} is the reference value (assigned value)
- u_{ref} is the standard uncertainty of the reference value
- u_{lab} is the standard uncertainty reported by a participant
- $\hat{\sigma}$ is the standard deviation for proficiency assessment

Both scores can be interpreted as: satisfactory result for $|\text{score}| \leq 2$, questionable result for $2 < |\text{score}| \leq 3$ and unsatisfactory result for $|\text{score}| > 3$.

z-score

The z -score compares the participant's deviation from the reference value with the standard deviation accepted for the proficiency test, $\hat{\sigma}$. Metrologically speaking, $\hat{\sigma}$ is the maximum acceptable standard uncertainty as defined by the organiser of the proficiency test. It is established by taking into account the acceptable laboratory uncertainty and potential contributions for homogeneity and stability. The Harmonised Protocol states that the method for homogeneity testing must be repeatable enough to render the homogeneity contribution negligible compared to the measurement uncertainty of the

laboratory [6]. Based on feedback from experts on the state-of-the-art and on discussions amongst the PT organisers, values for $\hat{\sigma}$ were set as 15 % of the assigned value for all measurands.

Should participants feel that these $\hat{\sigma}$ values are not fit for their purpose they can recalculate their scorings with a standard deviation matching their requirements.

ζ -score

The ζ -score states if the laboratory result agrees with the assigned value within the respective uncertainties. The ζ -score is the most relevant evaluation parameter, as it includes all parts of a measurement result, namely the expected value, its uncertainty and the unit of the result as well as the uncertainty of the assigned values. An unsatisfactory ζ -score might be due to an underestimation of the uncertainty, or to a large error causing a large deviation from the reference value, or to a combination of the two factors. A laboratory with an unsatisfactory ζ -score has an estimation of the uncertainty of its measurements which is not consistent with the laboratory's deviation from the reference value. Laboratories reporting a u_{lab} which is higher than $\hat{\sigma}$, have an analytical system in place which is not in agreement with the "state-of-the-art" for this matrix/analyte level combination.

Uncertainty evaluation

It is a well-established fact that uncertainty estimation is not trivial. Therefore an additional assessment was given as an indication of the plausibility of its uncertainty estimate for each laboratory providing an uncertainty: The standard uncertainty is most likely to fall in a range between a minimum uncertainty (u_{min}), and maximum allowed uncertainty (u_{max}). u_{min} is set to the standard uncertainty of the reference value. It is unlikely (but not impossible) that a laboratory carrying out the analysis on a routine basis could measure the measurand with a smaller uncertainty than the reference laboratory itself. u_{max} is set to the standard deviation accepted for the PT, $\hat{\sigma}$. If the standard uncertainty from the laboratory, u_{lab} , is smaller than u_{min} , the laboratory probably underestimated its uncertainty. However, this statement has to be taken with care as each laboratory will report only the uncertainty of its measurement, whereas the uncertainty of the reference value also includes contributions of homogeneity and stability. If those are large, measurement uncertainties smaller than u_{min} are possible and also plausible. If $u_{\text{lab}} > u_{\text{max}}$, the laboratory possibly overestimated the uncertainty. An evaluation of this statement can be made when looking at the comparison of the reported value and the assigned value: if the difference is small but the uncertainty is large, then overestimation is likely. If, however, the deviation is large but it is covered by the uncertainty, then the uncertainty was assessed correctly but is large. Naturally, this assessment will gain from pooling data from various intercomparisons. It should be pointed out that u_{max} is not a normative criterion: Which uncertainty is acceptable for a certain measurement is the decision of the customer of the respective result.

The standard uncertainty of the laboratory (u_{lab}) was calculated by dividing the reported expanded uncertainty by the reported coverage factor (k). When k was not specified, the reported expanded

uncertainty was considered as the half-width of a rectangular distribution; u_{lab} was then calculated by dividing this half-width by $\sqrt{3}$, as recommended by Eurachem and CITAC [7]. When no uncertainty was reported, it was set to zero ($u_{lab} = 0$).

9.4 Laboratory results and scorings

The results as reported by the participants are summarised in Annex 8 - 14. A table of the results together with the z-, ζ -scores and the uncertainty evaluation, and their graphical representation are provided. Laboratory codes were given randomly.

The results were also evaluated using Kernel density plots, useful to highlight sub-populations. These plots can be found in Annex 15. The software used to calculate Kernel densities was provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry [8].

Regarding the z- and ζ -scores, the results are summarised in Table 2. The laboratories' performances appear to be good for all measurands except for total As and Hg – the percentage of satisfying z-scores ranging between 67 % and 88 % for the former, and 54 % and 58 % for the latter, respectively. The picture looks not as promising for the ζ -score where the outcome is similar for all measurands – the satisfactory scores ranging between 52 % and 66 % and the unsatisfactory between 25 % and 33 %. It is however satisfying to see that for all measurands at least 50 % of the participants show a satisfying z- and ζ -score, except for total Hg where the percentage is 49 % (Table 2). Annex 16 summarises all scorings per laboratory and element.

Table 2 - Overview of scores with S(atisfactory), Q(uestionable) and U(nsatisfactory)

	n	z-scores						ζ -scores						z & ζ Satisfactory	
		S (#)	S (%)	Q (#)	Q (%)	U (#)	U (%)	S (#)	S (%)	Q (#)	Q (%)	U (#)	U (%)	(#)	(%)
Tot Cd	54	46	85 %	5	9 %	3	6 %	28	52 %	9	17 %	17	31 %	28	52 %
Extr Cd	36	31	86 %	1	3 %	4	11 %	23	64 %	4	11 %	9	25 %	22	61 %
Tot Pb	56	49	88 %	3	5 %	4	7 %	37	66 %	4	7 %	15	27 %	37	66 %
Extr Pb	37	28	76 %	1	3 %	8	22 %	21	57 %	3	8 %	13	35 %	21	57 %
Tot As	39	21	54 %	6	15 %	12	31 %	22	56 %	6	15 %	11	28 %	20	51 %
Tot Hg	45	26	58 %	9	20 %	10	22 %	24	53 %	6	13 %	15	33 %	22	49 %
Tot Sn	18	12	67 %	1	6 %	5	28 %	11	61 %	1	6 %	6	33 %	10	56 %

n – total number of laboratories having submitted results, # - number of laboratories

Although a high number of laboratories reported an uncertainty, which is good, there seems to be a general problem with the laboratories' estimation of the appropriate uncertainty, reflected by the outcome for the ζ -score and by the evaluation of the participants' uncertainties (Table 3).

Table 3 – Number of laboratories giving acceptable uncertainties (a) and uncertainties out of range (b and c)

	n	$u_{\min} \leq u_{\text{lab}} \leq u_{\max}$		$u_{\text{lab}} < u_{\min}$		$u_{\text{lab}} > u_{\max}$	
		a (#)	a (%)	b (#)	b (%)	c (#)	c (%)
Total Cd	54	30	56 %	15	28 %	9	17 %
Extractable Cd	36	26	72 %	3	8 %	7	19 %
Total Pb	56	31	55 %	17	30 %	8	14 %
Extractable Pb	37	17	46 %	12	32 %	8	22 %
Total As	39	2	5 %	23	59 %	14	36 %
Total Hg	45	17	38 %	12	27 %	16	36 %
Total Sn	18	1	6 %	9	50 %	8	44 %

n – total number of laboratories having submitted results, # - number of laboratories

The uncertainties' evaluation in Table 3 shows that for total As and Sn most participants' uncertainties were out of range, the share of acceptable uncertainties being below 10 % for both. Looking more specifically at the b and c scores, there seems to be a tendency to underestimate the uncertainty (b), rather than overestimate it (c), except for extractable Cd and total Hg. Laboratories must take into account that the uncertainty of a measurement frequently depends on the concentration range, so that when analysing trace elements present at low concentrations the uncertainty is higher. However, for total Sn, and especially for total As, the range of $u_{\min} - u_{\max}$ is more narrow than for the other measurands and thus it partly explains the low percentages for uncertainties within range.

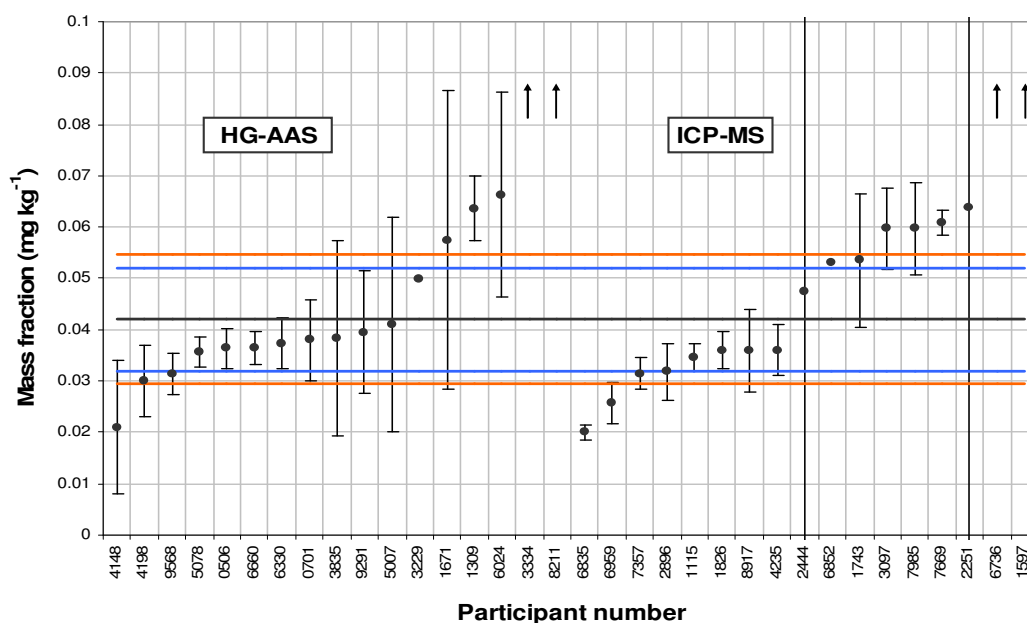
The overall outcome for total As is not satisfying as can be seen on the results graphs alone (Annex 12). The distribution of the means is not normal (see Kernel Graph, Annex 15), and there is a high number of very high reported mass fractions. It is well known that when analysing As by ICP-MS, $^{40}\text{Ar}^{35}\text{Cl}^+$, which has the same mass as As, could interfere. However, the problem does not seem to come from the instrumental method, since after comparing the results reported by laboratories using ICP-MS with those obtained by hydride generation-atomic absorption spectrometry (HG-AAS) no significant difference was observed (Fig 2). A contamination problem mainly coming from the reagents used for the analysis could be at the source of the overestimated As concentrations. Such a contamination problem would have an impact on the results due to the relatively low concentration of As in the test material.

A similar outcome, but not as pronounced as for total As, was observed for total Hg. Here too, the bias is probably due to a contamination problem, but could also be caused by the presence of interferences or problems in calibration at low concentrations.

Total Sn is included for the first time in an IMEP exercise. Of the eighteen participants having reported values for total Sn, 12 obtained a satisfactory z-score and 11 a satisfactory ζ -score. This is a promising result, considering the low concentration of Sn in the test material (0.062 mg kg^{-1}), compared to the maximum allowed levels given in the legislation for food ($50\text{-}200 \text{ mg kg}^{-1}$ depending on the food commodity), and the lack of experience of the laboratories. Furthermore, it should be emphasized that Sn is not a contaminant for which maximum levels have been set in the European legislation for

contaminants in feed [1]. Unfortunately it is not always possible to find naturally contaminated test material with appropriate concentrations for all the measurands covered in the ILC.

Fig 2 - Comparison of the results reported for total As according to the technique used.



9.5 Further information extracted from the questionnaire

Additional information was gathered from the questionnaire that participants were asked to fill in (Annex 7). Most of the answers are summarised in graphs in Annex 17 (use of recovery factor, uncertainty related questions, water content, method related questions, experience and use of reference material), or is otherwise highlighted in the following paragraphs.

Twelve participants corrected their results for recovery by one of the following options or a combination of them: nine used a certified reference material to evaluate the recovery and three by adding a known amount of the same analyte to the sample, and another three by doing both. Different justifications were given by those who did not correct for recovery and their reasons are listed in Table 4.

Table 4 – Reasons for not applying the recovery as reported in the questionnaire

Part Nr	Reasons for not applying recovery factor
0091	It was not necessary
0222	We have not a similar matrix Reference Material
0506	because we do not report results with recovery factor to customer
1115	Standard addition was found correctly.
1671	determination of VDLUFA (cf. position paper 2006)
1735	We do not correct the results for recovery in our results. Bias is lower to combined uncertainty
1743	We use certified reference material. We don't apply that recovery on our samples
1826	not part of method
2251	Difference between true value and mean value is acceptable.

Part Nr	Reasons for not applying recovery factor
2444	we use internal standards during the run
2688	based on experience there would be no gain in accuracy; difficult in trace analysis (homogeneity of sample!)
2699	Because the recovery of our Reference Material was included in the range 90-110 % and we didn't correct for the recovery as the CE 152/2009 norms
3097	Results for reference materials do not need any correction
3229	we have no
3334	Because we have a good recovery
4235	No bias
4418	We check our data with internal reference material with same matrix
5078	Validation results show 95-105% recoveries using certified reference materials.
5944	Because of shortage of testing material we decided not to perform recovery samples.
6024	From the validation data the estimated recovery is about 100%.
6330	The recovery factors were between 95-100% for all elements. We used certified reference material.
6852	The method was already tested several times and there is no need for R
7027	I used adding a known amount of the same analyte to the sample and using a certified reference material but we are not reporting recovery
7214	Recovery between 80 and 105 % in all cases.
7357	It is not a our routine every day procedure
7669	we're use recovery for quality control with accept range.
7985	We have used a certified reference material as quality control in per measurand
8211	Not common practice
9291	Not a custom. Incorporated in the uncertainty measurements
9763	out of standard

For uncertainty estimates, various combinations of one or more options were given (Q3, Annex 17). Seven laboratories gave a third method to base their uncertainty on – three used the "VDLUFA uncertainty estimate", one the Horwitz equation, one the calculation of the expanded uncertainty, one compared to a certified reference material and the last one applied the following formula : " $% U = 2 \times \text{square root of } (\% ubias^2 + \% uRw^2)$ ".

Eight participants have not corrected for the water content and gave the reasons listed in Table 5. One of the eight gave no reason, but a water content of '0'. The way in which the moisture content of the test material was to be calculated was described in detail in the sample accompanying letter.

Table 5 – Reasons for not applying water correction as reported in the questionnaire

Part Nr	Reasons
1115	less water content (3,9 %)
3229	-0.01
4041	-0.01
4235	Results were asked to report in mg/kg, i.s.o. mg/kg dry matter
7027	SR EN 14082:2003 ; not stipulated calculating the percentage of moisture.
7669	The customer not required.
7813	Analyses of metals was done from dry sample

Annex 18 gives information reported by the laboratories about their method of analysis when not having applied an official method.

All participants but five have a quality system in place based on ISO 17025, three have it combined with ISO 9000, and two have no quality system in place.

As for the sample treatment, seven participants used partial digestion, forty-six used total digestion and six gave no answer. When asked if they were accredited for the applied procedure, sixteen answered 'No' and forty 'Yes'.

Table 6 summarises the reference materials used for this type of analysis as reported by the participants.

Table 6 – Reference materials used by the participants as reported in the questionnaire

Part Nr	Which reference material?
0091	NIST 1547 Peach Leaves
0701	INCT-MPH-2, NCS ZC 80002b, NCS ZC 73009, NCS ZC73010
1115	NCS DC73348 Bush Branches and Leaves, NCS ZC73013 Spinage, NCS ZC73009 Wheat
1309	IAEA V 10 Hay Powder, NCS ZC 73013 Spinage, CTA-VTL-2 Tobacco Leaves
1597	Bipea ring test samples => precision, accuracy ..
1671	test sample from a interlaboratory comparison
1735	Cd, Pb, Sn RM for validation and QC, Hg for validation, QC and calibration
1743	1573a tomato leaves, cocoa powder
1826	NIST 1548a, NIST 8414, NIST 1573a
2251	DC73351, DC73350, Dorm-1, CRM129 Hay Powder
2849	Proficiency test material from
3097	BCR-402, NIST1547, NIST1570a
3334	MRC: FAPAS, Standards: Panreac
4041	Olea BCR N° 62
4148	VDLUFA test material
4198	NIST 1568a (Rice Flour), NIST 8418 (Wheat Gluten), NIST 1567a (Wheat Flour)
5007	mostly materials from ring tests
5041	NIST 1547
5086	Standard Solution 1000 mg/l
5944	CRM supplied by the Environment Canada, TM-26.3, lot 605
6330	Mixed Polish Herbs (INCT-MPH-2), NCS ZC 73016, standard solution for AAS: CHEM LAB NV, Sigma-Aldrich
6660	several CRM, SRM, local RM
6723	INCT-MPH-2
6835	Nist Durum Wheat Flour 84, INCT-MPH-2
7022	High Purity Standards (EPA Methods 200.7)
7813	Accu Trace, Merck, Carlo Erba, Aldrich, etc.
8442	standard solutions traceable to SRM from NIST
8917	Many, but in this instance NIST1547 peach leaves, NIST1548a total diet, NIST1570a spinach leaves
9034	CRM 189 for Pb and Cd, Pb 1000 mg/l SCP Science traceable to NIST 3128, Hg 1000 mg/l SCP Science traceable to NIST 3133, Cd 1000 mg/l Fluka product 36379
9611	standards MERCK
9763	LGC7173

Already at the very beginning of the exercise IMEP received comments from participants that the amount of test material distributed was too small. As consequence the protocol was reviewed and an email was sent to all participants giving specifications (Annex 19). Comments were also made in the questionnaire about the small amount of test material. For explanation - it is frequently said that the

outcome of proficiency tests does not reflect the real situation in analytical laboratories because participants do not treat PT test materials as they would treat normal samples. For instance participants in a PT would perform more replicates than in routine analysis. In order to check if that pre-assumption is correct, IMEP sent out the minimum amount of test material strictly needed to perform the requested analysis plus the water determination, without informing participants. Participants had to carefully plan the analysis to be performed in order to have enough test material. However, extra material was sent to the participants when requested if a reasonable justification was given, which was the case for three laboratories. All comments are listed in Table 7.

Table 7 – Comments as taken from the questionnaire

Part Nr	Comments
0091	For Hg determination acid digestion and pyrolysis followed by CVAAS do not agree and further checking is in progress. The results will be delivered in the beginning of January 2010.
1597	For us the partial extraction is the same as the procedure we use to report for total Cd, Pb that's why we gave the same results for Cd and Pb 'total' and 'extractable'. We are not accredited for As with ICP-MS, yet in the process of validation with the aim to get accredited in 2010.
1671	answers for question #7 are related to Pb and Cd; # 10 partial for Pb and Cd, total for As and Hg
1735	Sample was really short to produce al results in our normal procedure
2251	We do not want to participate in determination of Hg and extractable Cd/Pb. We have written
2444	The method for the determination of the total content, Rev Aqua Regia is under development, and we therefore don't have statistics i.e expansion factor for the method
2849	The sample material was very few. The whole procedure for analysis (three independent preparations for the elemental scope) had to be reviewed regarding the sample amount. Reproduction of the analysis might be necessary, but is impossible. Moreover, the content of arsenic and mercury seems to be extremely low. Sn is not within the scope of our feed investigations.
3198	We usually work with foodstuffs and our methods are accredited for them, not for animal feeds.
4198	This time the amount of sample was not enough to do the analysis correct.
5944	Addition to no.12+13: We participate in FAPAS proficiency tests mostly; but there is a lack in tests dealing with 'feed of plant origin' as well as in available CRM (quantity and certified heavy metals). So we wanted to take the opportunity to take part in this IMEP-29 test. But unfortunately the amount of material was too small for our routine methods determine total Cd, Pb, Hg and As.
6736	Reported uncertainty of our results was calculated in the following way: $u = t \cdot (s / \sqrt{n})$; where: t = value of Student t-test for (n-1) degrees of freedom and for confidence level of 95%; n = number of determinations (3); s = standard deviation; so our coverage factor $k=2.48$
6835	Our LOQ for As is 0,05 mg/kg, Hg 0,02 mg/kg Sn <0,05 mg/kg. The reported results for the elements are below our LOQ
7357	Total As results were strange, do not trust them, maybe some interferences
7669	The sample is too small quantity for testing follow your protocol.
9568	We had a contamination in extractable Pb, it was too little material to repeat.

10 Conclusion

In the IMEP-29 exercise, 59 out of 62 registered participants reported results, of which 27 reported for total Sn, which was included for the first time in an IMEP exercise. Between 68 % and 88 % satisfactory z-scores were achieved for all measurands except total As and Hg. It was very satisfying to observe that around 90 % of the participants reported an uncertainty with their results.

However, an effort is still needed to improve the evaluation of the uncertainties associated with the results, an observation triggered by the less good ζ -scores and the number of acceptable reported uncertainties ($u_{\min} \leq u_{\text{lab}} \leq u_{\max}$) ranging between 28 % and 72 % for all but two measurands. For total As and Sn the percentage of acceptable reported uncertainties was below 10 %, which is however partly explained by the small interval between u_{\min} and u_{\max} in these two cases.

Total As appeared to pose a problem in this exercise, as the results distribution showed a curve far from being normal and a tendency to very high mean values. This was also observed for total Hg, but to a smaller extent. This observation could not be explained by the instrumental technique used, but it is likely to be caused by contamination having a bigger impact at these low concentrations.

11 Acknowledgements

The Reference Materials Unit of IRMM is acknowledged for making available the test material and their support in the realisation of this exercise. The IMEP-group and Anne-Mette Jensen are thanked for revising the manuscript.

The laboratories participating in this exercise, listed below, are also kindly acknowledged.

ORGANISATION	COUNTRY
FAVV	Belgium
CODA-CERVA	Belgium
Agricultural University	Bulgaria
Food Inspection Centre for Physics & Chemistry of the Technology Centre of Liaoning Entry-Exit Inspection and Quarantine Bureau of the Peoples Republic of China	China
PANCHRIS Animal Premix LTD	Cyprus
EMPLA AG spol. s r.o.	Czech Republic
Laborator Morava, s.r.o.	Czech Republic
Eurofins Miljø A/S	Denmark
Evira	Finland
MTT Agrifood Research Finland	Finland
Chemisches und Veterinäruntersuchungsamt Ostwestfalen-Lippe	Germany
Universitaet Hohenheim	Germany
Institut fuer Hygiene und Umwelt	Germany
LAVES - Low. Saxony State Office for Consumer Protection and Food Safety	Germany
LTZ Augustenberg	Germany
LUFA Speyer	Germany
Thüringer Landesanstalt für Landwirtschaft	Germany
Landeslabor Berlin-Brandenburg	Germany
BfUL Leipzig	Germany
Landesbetrieb Hessisches Landeslabor	Germany
Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit	Germany
Agricultural & Environmental Testing & Research Laboratories SA	Greece
Food Allergens Laboratory	Greece
Health Service Executive	Ireland
Istituto Zooprofilattico Sperimentale della Puglia e della Basilicata	Italy
IZSLT	Italy
Istituto Zooprofilattico Sperimentale della Sicilia	Italy

IMEP-29: Total As, Cd, Pb, Hg and Sn, and extractable Cd and Pb in feed of plant origin

ORGANISATION	COUNTRY
IZS Sardegna	Italy
Istituto Zooprofilattico Sperimentale dell'Abruzzo e del Molise "G.Caporale"	Italy
CCL	Netherlands
Nutreco	Netherlands
Labnett Skien	Norway
National Veterinary Institute	Norway
Wojewódzka Stacja Sanitarno-Epidemiologiczna w Białymstoku	Poland
Wojewódzki Inspektorat Weterynarii Zakład Higieny Weterynaryjnej, Poznań	Poland
Inspekcja Weterynaryjna Wojewódzki Inspektorat Weterynarii w Szczecinie	Poland
Wojewódzki Inspektorat Weterynarii - Zakład Higieny Weterynaryjnej, Katowice	Poland
Ibprs Oddział Chłodnictwa i Jakości Żywności	Poland
Silesian University of Technology	Poland
ASAE	Portugal
ISQ - Instituto de Soldadura e Qualidade	Portugal
National Research Development Institute for Biology and Animal Nutrition - IBNA	Romania
D.S.V.S.A. Constanta	Romania
MOL joint stock company	Serbia
Jozef Stefan Institute	Slovenia
Laboratorio Agroalimentario de la Generalitat Valenciana	Spain
Trouw Nutrition España	Spain
Gobierno Vasco	Spain
Navarra de Servicio, S.A.	Spain
Junta de Castilla y León	Spain
Servicio de Laboratorio y Control. Sanidad y Servicios Ganaderos (TRAGSEGA S.A.)	Spain
SLU	Sweden
ALS Scandinavia AB	Sweden
Eurofins Food & Agro Sweden AB	Sweden
Coop Zentrallabor	Switzerland
UFAG Laboratorien AG	Switzerland
Central Laboratory (Thailand) Co., Ltd. Bangkok branch	Thailand
Betagro Public Co.,Ltd	Thailand
Food and Environment Research Agency	United Kingdom

Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
APLAC	Asia Pacific Laboratory Accreditation Cooperation
CRL-HM	Community Reference Laboratory for Heavy Metals in Feed and Food
CITAC	Co-operation for International Traceability in Analytical Chemistry
EA	European Co-operation for Accreditation
EC	European Commission
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
GUM	Guide to the Expression of Uncertainty in Measurement
HG-AAS	Hydride generation-atomic absorption spectrometry
ID-ICP-MS	Isotope dilution-inductively coupled plasma-mass spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
NRL	National Reference Laboratory
PT	Proficiency Test
SAS	Swiss Accreditation Service

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Annexes

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Annex 1 : Invitation to EA to nominate laboratories

Registration of participants is open until 15 November 2009. Distribution of the samples is foreseen for the second half of November 2009. In order to register, laboratories must:

1. **Enter their details online:**
<https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?seIComparison=340>
2. **Print the completed form when the system asks to do so**
Do not forget to clearly indicate on the printed form that you have been appointed by the European Cooperation for Accreditation to take part in this exercise **otherwise your laboratory will be invoiced for participation** normally applied for non-appointed laboratories.
3. **Send the printout to both the IMEP-29 and the EA-IMEP-29 coordinators:**

IMEP-29 coordinator Ms Ines Baer Fax +32 14 571 865 E-mail: jrc-irmm-imep@ec.europa.eu	EA-IMEP-29 coordinator Mr Ian Mann Fax +41 21 614 70 79 E-Mail: ian.mann@sfs.ch
--	--

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards



Ines Baer
IMEP-29 Coordinator

2



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements



Geel, 13 October 2009
JRC-D08/IBa/ve/ARES(2009)/276353

Mr Ian Mann
Federal Department of Economic Affairs FDEA
State Secretariat for Economic Affairs SECO
Swiss Accreditation Service SAS
Section Chemistry, Biology and Health
Agence pour la Suisse romande
Boulevard de Grancy 37
CH-1006 Lausanne
SWITZERLAND

Dear Ian,

Intercomparison for heavy metals in feed of plant origin

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison for the **"Determination of the total arsenic, cadmium, lead, mercury and tin, and of the extractable amount of cadmium and lead in feed of plant origin"**.

In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. They should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. There is a maximum number of 60 samples at your disposal, i.e. ca. 2 nominees per country.

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure.

Releaseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. <http://irmm.jrc.ec.europa.eu>
Telephone: direct line (32-14) 571 715. Fax: (32-14) 571 865.
E-mail: jrc-irmm-imep@ec.europa.eu

Annex 2 : Invitation to APLAC to nominate laboratories

2. **Print** the completed form when the system asks to do so
- Do not forget to clearly indicate on the printed form that you have been appointed by APLAC to take part in this exercise **otherwise your laboratory will be invoiced for participation** normally applied for non-appointed laboratories.

3. **Send** the printout to both the IMEP-29 and the APLAC coordinators:

IMEP-29 coordinator Ms Ines Baer Fax +32 14 571 865 E-mail: jrc-irmm-imep@ec.europa.eu	APLAC coordinator Mr Daniel Tholen Fax +1 231 941 9713 E-Mail: aplac.pt@gmail.com
--	---

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards



Ines Baer
IMEP-29 Coordinator

2



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements



Geel, 20 October 2009
JRC-D08/IBa/ve/ARES(2009)/285917

Mr Daniel Tholen
Chairman, APLAC PT Committee

Dear Daniel,

Intercomparison for heavy metals in feed of plant origin

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison for the "Determination of the total arsenic, cadmium, lead, mercury and tin, and of the extractable amount of cadmium and lead in feed of plant origin".

IRMM kindly invites APLAC to nominate 10-12 laboratories for free participation. However, they should hold (or be in the process of obtaining) an accreditation for this type of measurement. I suggest that you forward this invitation to a selection of specialised laboratories in this area.

Confidentiality of the participants and their results towards third parties is guaranteed.

Registration of participants is open until 15 November 2009. Distribution of the samples is foreseen for the second half of November 2009. Deadline for submission of results is 4 January 2010.

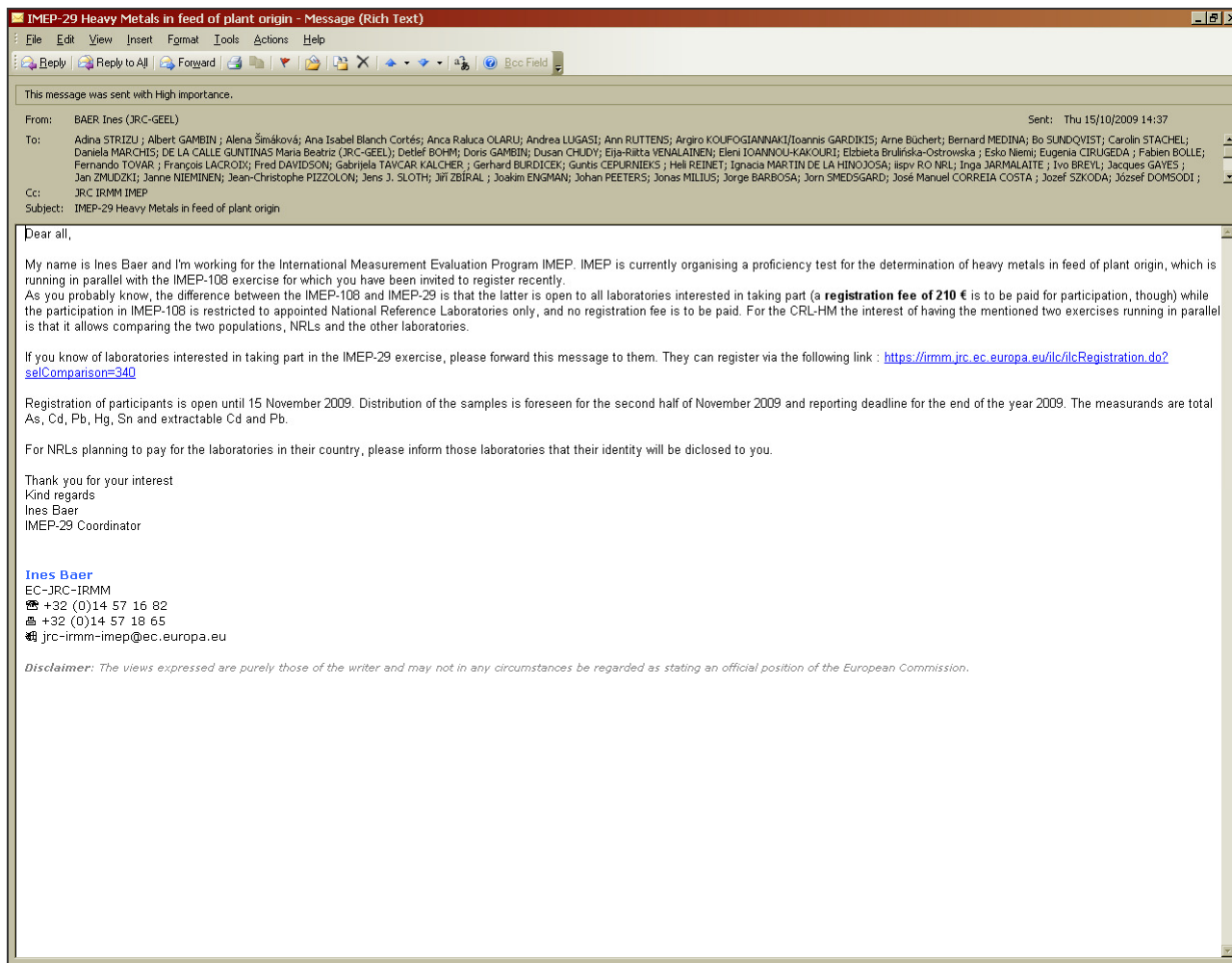
In order to register, laboratories must:

1. **Enter** their details online:

<https://irmm.jrc.ec.europa.eu/ile/ileRegistration.do?seComparison=340>

Bellevueweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. <http://irmm.jrc.ec.europa.eu>
Telephone direct line (32-14) 571 715. Fax: (32-14) 571 665.
E-mail: jrc-irmm-imep@ec.europa.eu

Annex 3 : Invitation sent to NRLs



Annex 4 : Announcement on IRMM - IMEP website

The screenshot shows a web browser window displaying the IRMM website. The header includes the European Commission logo and the text 'Joint Research Centre Institute for Reference Materials and Measurements'. The main content area features the IMEP logo and the title 'IMEP-29 Total As, Cd, Pb, Hg, Sn and extractable Cd and Pb in feed of plant origin'. The text describes the exercise, its purpose, and the cost. A table outlines the schedule for registration, sample dispatch, reporting of results, and the report to participants. The footer includes a 'Last Update' date of 19/11/2009.

IMEP-29 Total As, Cd, Pb, Hg, Sn and extractable Cd and Pb in feed of plant origin

The IMEP-29 exercise focuses on the analysis of total As, Cd, Pb, Hg, Sn and extractable Cd and Pb. This interlaboratory comparison runs in parallel to IMEP-108 where only appointed National Reference Laboratories can take part in.

This exercise is open to all laboratories, but only the first 60 registrations can be admitted.

The cost of this interlaboratory comparison is **EUR 210** per registration.

Test materials and analytes

The test material to be analysed is feed of plant origin contained in a brown glass bottle. Each participant will receive one bottle. the measurands are total As, Cd, Pb, Hg, Sn and extractable Cd and Pb.

General outline of the exercise

Participants are requested to perform 1-3 independent analyses using the method of their choice.

Schedule

Registration	Sample dispatch	Reporting of results	Report to participants
deadline 15/11/2009	2nd half of November 2009	deadline 04/01/2010	March 2010

Last Update 19/11/2009

Annex 5 : Sample accompanying letter

2. Add 85 mL of a 5 % (w/w) HNO₃ solution (see note for the preparation of the HNO₃ solution).
3. Cover the beaker with a watch-glass and boil for 30 min on a hot plate (make sure that the plate warms up homogeneously all over the surface).
4. Allow to cool. Decant the liquid into a 100 mL volumetric flask, rinsing the beaker and the watch-glass several times with 5 % (w/w) HNO₃.
5. Dilute to the mark with 5 % (w/w) HNO₃.
6. After homogenising, filter through a dry folded filter paper into a dry container. Use the first portion of the filtrate to rinse the glassware and discard that part. If the determination is not carried out immediately, the container with filtrate shall be stoppered.
7. Carry out a blank test at the same time as the extraction, with only the reagents and follow the same procedure as for the samples.

To construct the calibration curve dilute the standards in 5 % (w/w) HNO₃.

NOTE: To prepare 1 kg stock of 5 % (w/w) HNO₃ (density ~ 1.0257 kg/l): mix 77 g of 65 % (w/w) HNO₃ with 923 g water. Use a balance of two digits for the weighing.

For the determination of the **total** content of Cd, Pb, As, Hg and Sn the procedure used for the analyses should resemble as closely as possible the one that you use in routine sample analysis.

The results are to be reported referring to dry mass and thus corrected for humidity. To calculate the water content in the test material, please apply the following procedure:

Weigh 2 g of test material and dry it at 103 ± 2 °C for 4 hours in triplicate

Please perform two or three independent measurements per measurand. Correct the measurement results for recovery, and report the corrected values, plus their mean on the reporting website. The results should be reported in the same form (e.g., number of significant figures) as those normally reported to the customer.

You can find the reporting website at <https://irmm.jrc.ec.europa.eu/irrmcReporting.do>. To access this webpage you need a personal password key, which is: «Part_key». The system will guide you through the reporting procedure. Please enter for each parameter:

- In the spaces allocated for "measurement 1" to "measurement 3", the measurement results and the technique you used, but not the uncertainty for each individual measurement
- In the space allocated for "measurement 4": the mean of the results, the technique you used, and the uncertainty of the mean, including the expansion factor.

After entering all results, please also complete the relating questionnaire. Do not forget to save, submit and confirm always when required.

Directly after submitting your results and the questionnaire information online, you will be prompted to print the completed report form. Please do so, sign the paper version and return it to IRMM by fax or by e-mail. Check your results carefully for any errors before submission, since this is your definitive confirmation.

The deadline for submission of results is 03/01/2010.

«Part_key»



Geel, 18 November 2009
JRC.D08/IBA/ve/ARES(2009)/328789

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«ADDRESS4»
«ZIP» «TOWN»
«COUNTRY»

Participation to IMEP-29, a proficiency test exercise for the determination of total arsenic, cadmium, lead, mercury and tin, and of the extractable amount of cadmium and lead in feed of plant origin

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-29 intercomparison for the determination of total As, Cd, Pb, Hg and Sn, and of the extractable amount of Cd and Pb in feed of plant origin.

This parcel contains:

- a) One bottle containing 10 g of the test material
- b) A "Confirmation of Receipt" form
- c) This accompanying letter

Please check whether the bottle containing the test material remained undamaged during transport. Then, please send the "Confirmation of receipt" form back (fax: +32-14-571 865; e-mail: jrc-irmm-imep@ec.europa.eu). You should store the samples in a dark and cold place (not more than 18 °C) until analysis.

The measurands are: total As, Cd, Pb, Hg and Sn, and extractable Cd and Pb according to Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed, in feed of plant origin.

The determination of the extractable amounts of Cd and Pb shall be carried out by strictly applying the following procedure:

Protocol for the partial extraction of Cd and Pb in feed of plant origin
(IMEP-29)

1. Weigh about 2 g of the prepared test sample to the nearest 1 mg into a 250 mL beaker.

Ref:esweg 111, B-2440 Geel - Belgium, Telephone: (32-14) 571 211, <http://irmm.jrc.ec.europa.eu>
Telephone: direct line (32-14) 571 862, Fax: (32-14) 571 865
E-mail: jrc-irmm-imep@ec.europa.eu

«Part_key»

Please keep in mind that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies and analysts alike.

Your participation in this project is greatly appreciated. If you have any remaining questions, please contact me by e-mail:

JRC-IRMM-IMEP@ec.europa.eu

With kind regards



Dr. Ines Baer
IMEP-29 Co-ordinator

Enclosures: 1) one bottle containing the test material; 2) confirmation of receipt form; 3) Accompanying letter.

Cc: F. Ulberth

Annex 6 : 'Confirmation of receipt' form



EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Isotope measurements

Annex to JRC.D08/IBa/ive/ARES(2009)/328789

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«Address4»
«ZIP» «TOWN»
«COUNTRY»

IMEP-29

total Cd, Pb, As, Hg and Sn and
extractable amounts of Cd and Pb in feed of plant origin

Confirmation of receipt of the samples

***Please return this form at your earliest convenience.
This confirms that the sample package arrived.
In case the package is damaged,
please state this on the form and contact us immediately.***

ANY REMARKS

Date of package arrival

Signature

Please return this form to:

Dr Ines Baer

IMEP-29 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

Fax : +32-14-571865
e-mail : jrc-irmm-imep@ec.europa.eu

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. <http://irmm.jrc.ec.europa.eu>
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.

E-mail: jrc-irmm-imep@ec.europa.eu



Annex 7 : Questionnaire

1. Did you apply a recovery factor to correct your measurement results?

☐ no
☐ yes

1.1. If Yes, what are the recovery factors (R, in %) you used:

1.1.1. for Cd (in %)

1.1.2. for Pb (in %)

1.1.3. for As (in %)

1.1.4. for Hg (in %)

1.1.5. for Sn (in %)

1.2. If Yes, did you determine R by:

☐ 1. adding a known amount of the same analyte to the sample
☐ 2. using a certified reference material
☐ 3. other

1.3. If no, please state why?

2. What is the level of confidence reflected by the coverage (k) factors stated above? (in %)

3. What is the basis of your uncertainty estimate (multiple answers are possible)?

☐ 1. uncertainty budget calculated according to iso-gum
☐ 2. known uncertainty of the standard method
☐ 3. uncertainty of the method as determined in-house validation
☐ 4. measurement of replicates (i.e. precision)
☐ 5. expert guesstimate
☐ 6. use of intercomparison data
☐ 7. other

3.1. If other, please specify

4. Do you usually provide an uncertainty statement to your customers for this type of analysis?

☐ no
☐ yes

5. Did you correct for the water content of the sample?

☐ no
☐ yes

5.1. If Yes, what is the water content (in % of the sample mass)?

5.2. If no, what was the reason not to do this?

6. Did you modify the prescribed protocol for the partial digestion?

☐ no
☐ yes

6.1. If yes, please specify the modifications introduced

7. Did you analyse the sample according to an official method?

☐ no
☐ yes

7.1. If no, please describe (in max. 150 characters for each reply) your

7.1.1. sample pre-treatment

7.1.2. digestion step

7.1.3. extraction / separation step

7.1.4. instrument calibration step

7.2. If Yes, which:

8. Does your laboratory carry out this type of analysis (as regards the analytes, matrix and methods) o

☐ no

☐ yes

8.1. If Yes, please estimate the number of samples (As, Cd, Pb, Hg, Sn measurements together):

☐ a) 0-50 samples per year

☐ b) 50-250 samples per year

☐ c) 250-1000 samples per year

☐ d) more than 1000 samples per year

9. Does your laboratory have a quality system in place?

☐ no

☐ yes

9.1. If Yes, which:

☐ a) ISO 17025

☐ b) ISO 9000 series

☐ c) Other

9.1.1. If other, please specify

9.2. If yes, are you accredited?

☐ No

☐ Yes

9.2.1. If yes, by which Accreditation Body have you been accredited?

10. Which type of sample treatment do you routinely use for such samples?

☐ partial digestion (according to the legislation)

☐ total digestion

11. Is your laboratory accredited for the sample treatment that you specify in question 10?

☐ No

☐ Yes

12. Does your laboratory take part in an interlaboratory comparison for this type of analysis on a regular basis

☐ no

☐ yes

12.1. If yes, which one(s)

13. Does your laboratory use a reference material for this type of analysis?

☐ no

☐ yes

13.1. If YES, is the material used for the validation of procedures?

☐ no

☐ yes

13.2. If YES, is the material used for calibration of instruments?

☐ no

☐ yes

13.3. If yes, which one(s)

14. Do you have any comments? Please let us know: ...

Annex 8 : Results for Total Cadmium

X_{ref} = 0.120 and U_{ref} = 0.007; all values are given in (mg kg⁻¹)

Part Nr	x1	x2	x3	x4	U _{lab}	k ^a	Mean (x _{lab})	u _{lab}	Technique	z ^b	ζ ^b	Unc ^c
0091	0.114	0.118	0.111		0.005	1	0.114	0.005	ICP-MS	-0.3	-0.9	a
0222	0.119	0.119	0.110		0.008	2	0.116	0.004	ICP-MS	-0.2	-0.8	a
0529	0.099	0.112	0.114		10	√3	0.108	6	ETAAS	-0.6	0.0	c
0701	0.161	0.169			0.020	1.28	0.165	0.016	FAAS	2.5	2.8	a
1115	0.111	0.106	0.107	0.109	0.0051	√3	0.108	0.0029	ICP-MS	-0.7	-2.6	b
1309	0.093	0.094	0.091		0.061	2	0.093	0.031	ETAAS	-1.5	-0.9	c
1597	<0.15	<0.15	<0.15	<0.15					ETAAS			
1671	0.113	0.114			0.028	2	0.114	0.014	ICP-MS	-0.4	-0.5	a
1735	0.095	0.092	0.095		0.018	2	0.094	0.009	ICP-AES	-1.4	-2.7	a
1743	0.123	0.123	0.123		0.005	√3	0.123	0.003	ICP-MS	0.2	0.7	b
1826	0.112	0.103	0.104		0.015	2	0.106	0.008	ICP-MS	-0.8	-1.7	a
2251	0.1175	0.1185	0.1169		19	2	0.1176	10	ICP-MS	-0.1	0.0	c
2444	0.099	0.112	0.105		0.010	√3	0.105	0.006	ICP-MS	-0.8	-2.2	a
2688	0.100	0.103	0.106		0.022	√3	0.103	0.013	ICP-AES	-0.9	-1.3	a
2699	0.115	0.119	0.118		0.020	√3	0.117	0.012	FAAS	-0.1	-0.2	a
2849	0.124	0.122	0.108		0.059	√3	0.118	0.034	ICP-MS	-0.1	-0.1	c
2896	0.104	0.107	0.103		0.030	2	0.105	0.015	ICP-MS	-0.9	-1.0	a
3097	0.129	0.131	0.125		0.020	2	0.128	0.010	ICP-MS	0.5	0.8	a
3102	0.100	0.095	0.105		0	√3	0.100	0	ETAAS	-1.1	-5.7	b
3198	0.097	0.097	0.094		0.020	2	0.096	0.010	FAAS	-1.3	-2.3	a
3229	0.102	0.097	0.098	0.101	0	√3	0.100	0	ETAAS	-1.1	-5.9	b
3334	0.10	0.11			0	√3	0.11	0	HG-AAS	-0.8	-4.3	b
3835	0.115	0.114	0.111		0.056	2	0.113	0.028	ETAAS	-0.4	-0.2	c
4148	0.093	0.099	0.097		0.003	√3	0.096	0.002	AAS graphit	-1.3	-6.1	b
4198	0.126	0.125			0.001	2	0.126	0.001	Graphite-furnace AAS	0.3	1.6	b
4235	0.114	0.110			0.018	2	0.112	0.009	ICP-MS	-0.4	-0.8	a
4418	0.107				0.021	2	0.107	0.011	ICP-AES	-0.7	-1.2	a
5007	0.114	0.116	0.120		0.056	2	0.117	0.028	ICP-MS	-0.2	-0.1	c
5041	0.104	0.0970			0.020	2	0.101	0.010	HR-ICP-MS	-1.1	-1.9	a
5048	0.3094				0.019	√3	0.3094	0.011	FAAS	10.5	16.4	a
5078	0.113	0.106	0.115		0.006	2	0.111	0.003	ICP-MS	-0.5	-1.9	b
5944	0.11	0.11			0.002	√3	0.11	0.001	ETAAS	-0.6	-2.7	b
6024	0.085	0.083	0.079		0.016	2	0.082	0.008	FAAS	-2.1	-4.3	a
6330	0.174	0.149	0.180		0.015	2	0.168	0.008	ETAAS	2.6	5.8	a
6660	0.113	0.109	0.108		0.007	2	0.110	0.004	ICP-MS	-0.6	-2.0	a
6723	0.081				0.02	2	0.081	0.01	FAAS	-2.2	-3.7	a
6736	0.116	0.100	0.110		0.020	2.48	0.109	0.008	ICP-AES	-0.6	-1.3	a
6814	<0.5	<0.5	<0.5	<0.5					ICP-AES			
6835	0.106	0.111	0.106		0.0029	1	0.108	0.0029	ICP-MS	-0.7	-2.7	b
6852				0.108	0	√3	0.108	0	ICP-MS	-0.7	-3.4	b
6959	0.109	0.109	0.114		0.004	2	0.111	0.002	ICP-MS	-0.5	-2.3	b
7022	0.16	0.14	0.15		0.01	2	0.15	0.01	ICP-AES	1.7	4.9	a
7027	0.097	0.091	0.089		0.0184	2	0.092	0.0092	FAAS	-1.5	-2.8	a
7214	0.08	0.09			0	√3	0.09	0	ETAAS	-1.9	-10.0	b
7357	0.100	0.096	0.095		0.008	2	0.097	0.004	ICP-MS	-1.3	-4.3	a
7669	0.1017	0.1028	0.1047		0.0035	2	0.1031	0.0018	ICP-MS	-0.9	-4.3	b
7813	0.10	0.11	0.11		0.03	2	0.11	0.015	AAS furnace technique	-0.7	-0.9	a
7985	0.102	0.096	0.098		0.011	2	0.099	0.006	ICP-MS	-1.2	-3.3	a
8211	0.215	0.221	0.209		0.039	2	0.215	0.020	HGA-AAS (furnace oven)	5.3	4.8	c
8442	0.15	0.15	0.14		0.05	2	0.15	0.03	ETAAS	1.5	1.1	c
8917	0.114	0.111	0.109		0.022	2	0.111	0.011	ICP-MS	-0.5	-0.8	a
9034	0.11	0.12	0.11		0.04	2	0.11	0.02	ETAAS	-0.4	-0.3	c
9291	0.11	0.12			0.02	√3	0.12	0.01	ETAAS	-0.3	-0.4	a
9568	0.137	0.135	0.130		0.015	√3	0.134	0.009	ICP-MS	0.8	1.5	a
9611	0.074	0.082	0.083		0.011	100	0.080	0.000	ETAAS	-2.2	-11.5	b
9763	0.91	0.91	0.91		0.01	2	0.91	0.01	FAAS	43.9	129.4	a

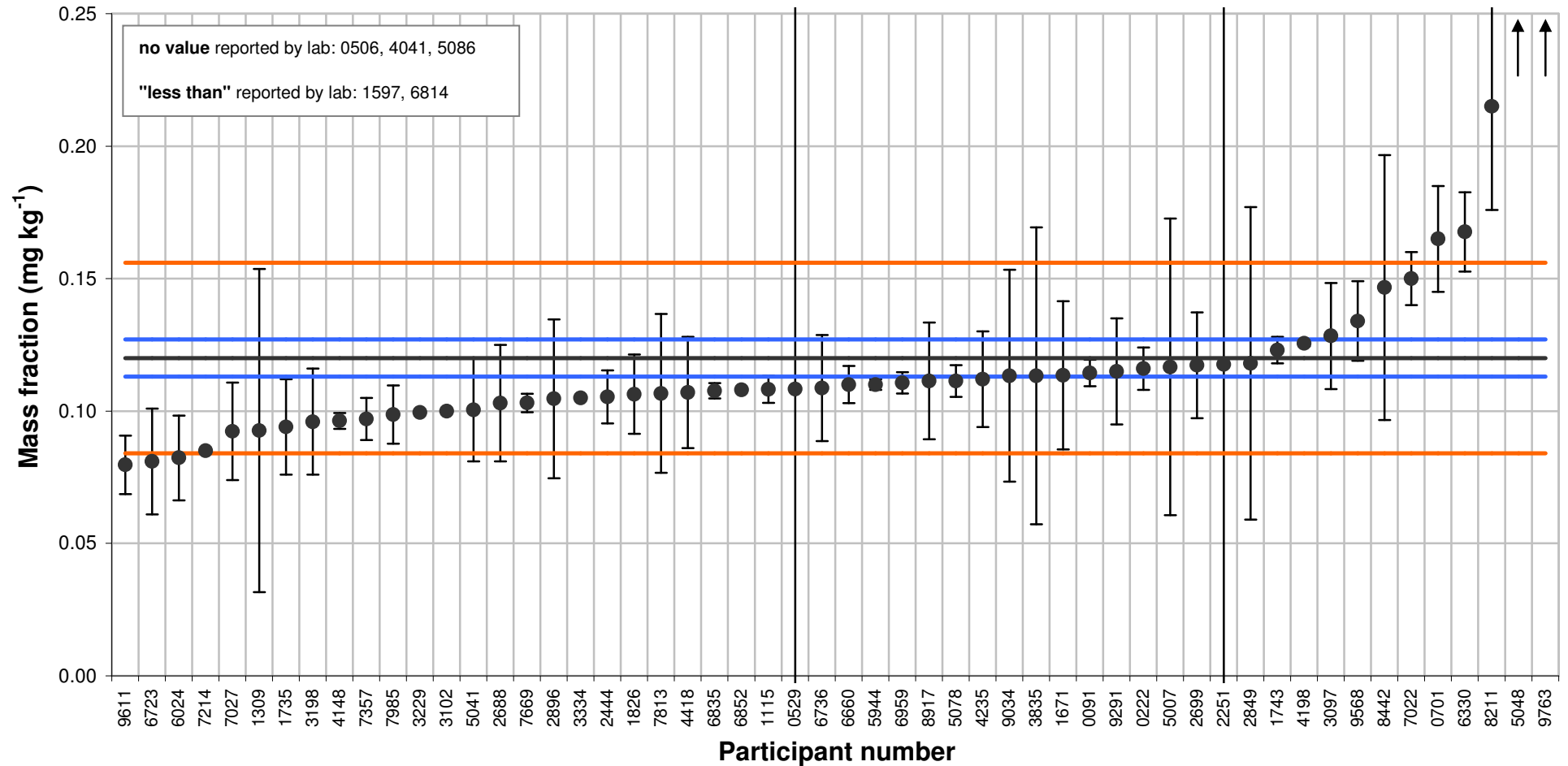
^a √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

^b Satisfactory, Questionable, Unsatisfactory

^c Where: **a** = $u_{\min} \leq u_{\text{lab}} \leq u_{\max}$, **b** : $u_{\text{lab}} < u_{\min}$, and **c** : $u_{\text{lab}} > u_{\max}$

IMEP-29 (Heavy metals in feed of plant origin): Total Cadmium

Certified value: $X_{\text{ref}} = 0.121 \text{ mg} \cdot \text{kg}^{-1}$; $U_{\text{ref}} = 0.007 \text{ mg} \cdot \text{kg}^{-1}$ ($k=2$)



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.

The thick black line corresponds to X_{ref} , the blue lines mark the boundary of the reference interval ($X_{\text{ref}} \pm 2U_{\text{ref}}$), and the orange lines that of the target interval ($X_{\text{ref}} \pm 2\sigma$).

Annex 9 : Results for Extractable Cadmium

$X_{ref} = 0.114$ and $U_{ref} = 0.003$; all values are given in (mg kg⁻¹)

Part Nr	x1	x2	x3	x4	U _{lab}	k ^a	Mean (x _{lab})	u _{lab}	Technique	z ^b	ζ ^b	Unc ^c
0529	0.0605	0.0560	0.0660	0.0610	10	√3	0.0609	5.7735	ETAAS	-3.1	0.0	c
1115	0.109	0.105	0.102		0.0087	√3	0.105	0.0050	ICP-MS	-0.5	-1.7	a
1309	0.076	0.084			0.054	2	0.08	0.027	ETAAS	-2.0	-1.3	c
1597	<0.15	<0.15	<0.15	<0.15					ETAAS			
1671	0.128	0.121	0.121		0.031	2	0.123	0.016	ICP-MS	0.5	0.6	a
1735	0.115	0.110			0.022	2	0.113	0.011	ICP-AES	-0.1	-0.1	a
1743	0.119	0.121	0.120	0.119	0.003	√3	0.120	0.002	ICP-MS	0.3	2.5	a
1826	0.109	0.107	0.105		0.016	2	0.107	0.008	ICP-MS	-0.4	-0.9	a
2444	0.101	0.105			0.007	2	0.103	0.004	ICP-MS	-0.6	-2.9	a
2699	0.089	0.089	0.091		0.015	√3	0.090	0.009	FAAS	-1.4	-2.8	a
2849	0.115	0.114	0.117		0.058	√3	0.115	0.033	ICP-MS	0.1	0.0	c
2896	0.0993	0.0996	0.0991	0.0994	0.0067	2	0.0994	0.0034	ICP-MS	-0.9	-4.0	a
3097	0.113	0.106			0.018	2	0.110	0.009	ICP-MS	-0.3	-0.5	a
3835	0.114	0.116	0.121		0.058	2	0.117	0.029	ETAAS	0.2	0.1	c
4198	0.111	0.114			0.001	2	0.113	0.001	Graphite-furnace AAS	-0.1	-1.0	b
4235	0.107	0.103			0.017	2	0.105	0.009	ICP-MS	-0.5	-1.0	a
5007	0.123	0.124	0.121		0.06	2	0.123	0.03	ICP-MS	0.5	0.3	c
5041	0.102	0.0962			0.020	2	0.0991	0.010	HR-ICP-MS	-0.9	-1.5	a
5078	0.121	0.120	0.119		0.006	2	0.120	0.003		0.4	1.8	a
5944	0.09	0.10			0.003	√3	0.10	0.002	ETAAS	-1.1	-8.4	a
6330	0.086	0.098			0.008	2	0.092	0.004	ETAAS	-1.3	-5.2	a
6660	0.108	0.117	0.121		0.016	2	0.115	0.008	ICP-MS	0.1	0.2	a
6723	0.052				0.015	2	0.052	0.0075	FAAS	-3.6	-8.1	a
6736	0.108	0.104	0.099		0.010	2.48	0.104	0.004	ICP-AES	-0.6	-2.4	a
6835	0.109	0.111	0.126		0.0093	1	0.115	0.0093	ICP-MS	0.1	0.1	a
6852				0.133	0	√3	0.133	0	ICP-MS	1.1	13.1	b
7022	0.12	0.14	0.13		0.01	2	0.13	0.005	ICP-AES	0.9	3.1	a
7669	0.1129	0.1141			0.0109	2	0.1135	0.0055	ICP-MS	0.0	-0.1	a
7813	0.08	0.09	0.08	0.09	0.03	2	0.09	0.02	AAS furnace technique	-1.7	-1.9	a
7985	0.112	0.118	0.104		0.011	2	0.111	0.006	ICP-MS	-0.2	-0.5	a
8211	0.181	0.181	0.188		0.033	2	0.183	0.017	HGA-AAS (furnace oven)	4.1	4.2	a
8442	0.14	0.15	0.16		0	√3	0.15	0	ETAAS	2.1	24.8	b
8917	0.098	0.099	0.101	0.100	0.020	2	0.100	0.010	ICP-MS	-0.8	-1.4	a
9034	0.12	0.14	0.15		0.06	2	0.14	0.03	ETAAS	1.3	0.8	c
9291	0.11	0.11			0.02	2	0.11	0.01	ETAAS	-0.2	-0.4	a
9568	0.124	0.122	0.118		0.15	√3	0.121	0.09	ICP-MS	0.4	0.1	c
9611	<0.01	<0.01	<0.01	<0.01					ETAAS			
9763	0.49	0.49	0.49		0.02	2	0.49	0.01	FAAS	22.0	37.2	a

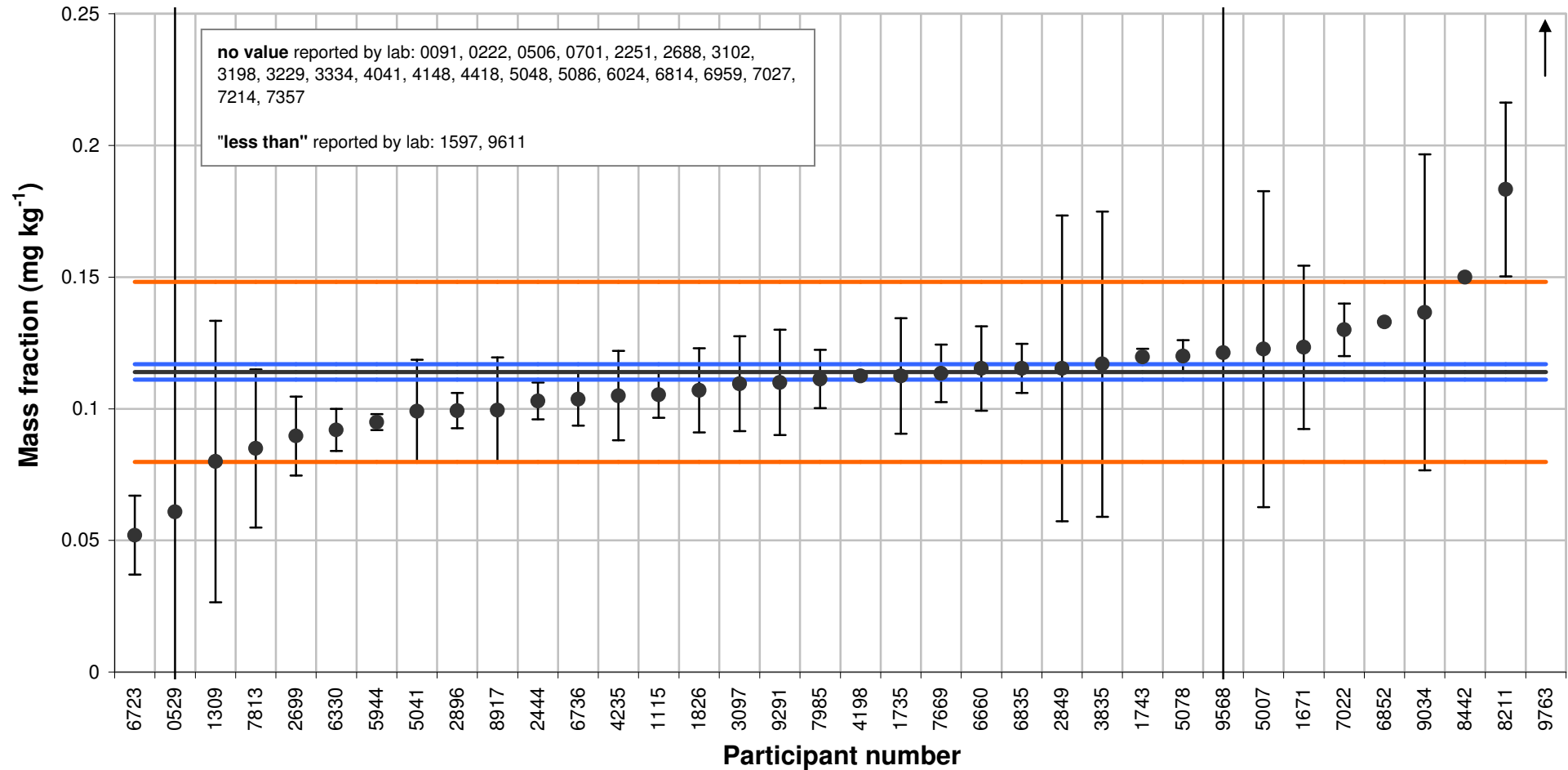
^a √3 is set by the ILC coordinator when no expansion factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with $k=√3$. For explanation see Ch 9.3

^b Satisfactory, Questionable, Unsatisfactory

^c Where: **a** = $U_{min} \leq U_{lab} \leq U_{max}$, **b** : $U_{lab} < U_{min}$, and **c** : $U_{lab} > U_{max}$

IMEP-29 (Heavy metals in feed of plant origin): Extractable Cadmium

Certified value: $X_{\text{ref}} = 0.114 \text{ mg} \cdot \text{kg}^{-1}$; $U_{\text{ref}} = 0.0029 \text{ mg} \cdot \text{kg}^{-1}$ ($k=2$)



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.

The thick black line corresponds to X_{ref} , the blue lines mark the boundary of the reference interval ($X_{\text{ref}} \pm 2U_{\text{ref}}$), and the orange lines that of the target interval ($X_{\text{ref}} \pm 2\sigma$).

Annex 10 : Results for Total Lead

$X_{ref} = 1.67$ and $U_{ref} = 0.11$; all values are given in (mg kg⁻¹)

Part Nr	x1	x2	x3	x4	U _{lab}	k ^a	Mean (x _{lab})	u _{lab}	Technique	z ^b	ζ ^b	Unc ^c
0091	1.73	1.69	1.85		0.12	1	1.76	0.12	ICP-MS	0.3	0.7	a
0222	1.71	1.59	1.83		0.15	2	1.71	0.08	ICP-MS	0.2	0.4	a
0529	1.602	1.762	1.680		10	√3	1.681	6	ETAAS	0.0	0.0	c
0701	1.36	1.31			0.17	1.10	1.34	0.15	FAAS	-1.3	-2.0	a
1115	1.565	1.567	1.607		0.033	√3	1.580	0.019	ICP-MS	-0.4	-1.6	b
1309	1.41	1.53	1.40		0.58	2	1.45	0.29	ETAAS	-0.9	-0.8	c
1597	1.139	1.505	1.118		0.7	2	1.3	0.4	ETAAS	-1.7	-1.2	c
1671	1.58	1.60			0.40	2	1.59	0.20	ICP-MS	-0.3	-0.4	a
1735	1.43	1.37	1.47		0.28	2	1.42	0.14	ICP-AES	-1.0	-1.6	a
1743	1.570	1.564	1.532		0.1	√3	1.6	0.1	ICP-MS	-0.5	-1.4	a
1826	1.64	1.57	1.55		0.16	2	1.59	0.08	ICP-MS	-0.3	-0.9	a
2251	1.673	1.690	1.661		10	2	1.675	5	ICP-MS	0.0	0.0	c
2444	1.646	1.671	1.658		0.018	√3	1.658	0.010	ICP-MS	0.0	-0.2	b
2688	1.275	1.234	1.312	1.273	0.190	√3	1.274	0.110	ICP-AES	-1.6	-3.2	a
2699	1.761	1.770	1.754		0.335	√3	1.762	0.193	FAAS	0.4	0.5	a
2849	1.71	1.70	1.69		0.85	√3	1.70	0.49	ICP-MS	0.1	0.1	c
2896	1.47	1.45	1.48		0.18	2	1.47	0.09	ICP-MS	-0.8	-1.9	a
3097	1.893	1.901	1.815		0.281	2	1.870	0.141	ICP-MS	0.8	1.3	a
3102	0.36	0.37	0.38	0.36	0	√3	0.37	0	ETAAS	-5.2	-23.7	b
3198	1.53	1.62			0.33	2	1.58	0.17	ETAAS	-0.4	-0.5	a
3229	1.84	1.63	1.78	1.72	0	√3	1.74	0	ETAAS	0.3	1.3	b
3334	1.8	1.9			0	√3	1.9	0	HG-AAS	0.7	3.3	b
3835	1.77	1.961	1.824		0.46	2	1.852	0.23	ETAAS	0.7	0.8	a
4148	1.479	1.466	1.458		0.02	√3	1.468	0.01	AAS graphit	-0.8	-3.6	b
4198	1.610	1.612			0.001	2	1.611	0.001	Graphite-furnace AAS	-0.2	-1.1	b
4235	1.548	1.531			0.600	2	1.540	0.300	ICP-MS	-0.5	-0.4	c
4418	1.582				0.316	2	1.582	0.158	ICP-AES	-0.4	-0.5	a
5007	1.750	1.784	1.792		0.89	2	1.775	0.45	ICP-MS	0.4	0.2	c
5041	1.46	1.44			0.29	2	1.45	0.15	HR-ICP-MS	-0.9	-1.4	a
5048	1.9288				0.051	√3	1.9288	0.029	FAAS	1.0	4.1	b
5078	1.82	1.70	1.81		0.196	2	1.78	0.098	ICP-MS	0.4	0.9	a
5086	3.26	3.41	3.45	3.36	0.22	√3	3.37	0.13	FAAS	6.8	12.3	a
5944	2.3	2.1			0.18	√3	2.2	0.10	ETAAS	2.1	4.5	a
6024	1.26	1.33	1.13		0.25	2	1.24	0.13	FAAS	-1.7	-3.1	a
6330	1.329	1.154	1.518	1.333	0.160	2	1.334	0.080	ETAAS	-1.3	-3.5	a
6660	1.69	1.68	1.72		0.06	2	1.70	0.03	ICP-MS	0.1	0.4	b
6723	1.421				0.331	2	1.421	0.166	FAAS	-1.0	-1.4	a
6736	1.69	1.82	1.60		0.27	2.48	1.70	0.11	ICP-AES	0.1	0.3	a
6814	1.13	1.07	0.97	1.05	0	√3	1.06	0	ICP-AES	-2.5	-11.2	b
6835	1.52	1.58	1.53	1.55	0.038	1	1.55	0.038	ICP-MS	-0.5	-1.9	b
6852	1.65				0	√3	1.65	0	ICP-MS	-0.1	-0.4	b
6959	1.761	1.738	1.782		0.036	2	1.760	0.018	ICP-MS	0.4	1.6	b
7027	1.56	1.50	1.60		0.3106	2	1.553	0.1553	FAAS	-0.5	-0.7	a
7214	1.57	1.52			0	√3	1.55	0	ETAAS	-0.5	-2.3	b
7357	1.44	1.43	1.42		0.24	2	1.43	0.12	ICP-MS	-1.0	-1.8	a
7669	1.4457	1.4130	1.4005		0.0197	2	1.4197	0.0099	ICP-MS	-1.0	-4.5	b
7813	0.64	0.63	0.65		0.02	2	0.64	0.01	AAS furnace technique	-4.1	-18.4	b
7985	1.87	1.96	1.92		0.13	2	1.92	0.07	ICP-MS	1.0	2.9	a
8211	3.465	3.381	3.661		0.876	2	3.502	0.438	HGA-AAS (furnace oven)	7.3	4.2	c
8442	2.37	2.33	2.19	2.29	0.4	2	2.30	0.2	ETAAS	2.5	3.0	a
8917	1.55	1.56	1.54		0.20	2	1.55	0.10	ICP-MS	-0.5	-1.1	a
9034	2.1	1.9	2.0		0.3	2	2.0	0.2	ETAAS	1.3	2.1	a
9291	1.3	1.4			0.42	2	1.4	0.21	ETAAS	-1.3	-1.5	a
9568	1.67	1.67	1.67		0.2	√3	1.67	0.1	ICP-MS	0.0	0.0	a
9611	1.115	1.166	1.199		0.15	100	1.160	0.00	ETAAS	-2.0	-9.3	b
9763	2.15	1.96	2.10		0.20	2	2.07	0.10	FAAS	1.6	3.5	a

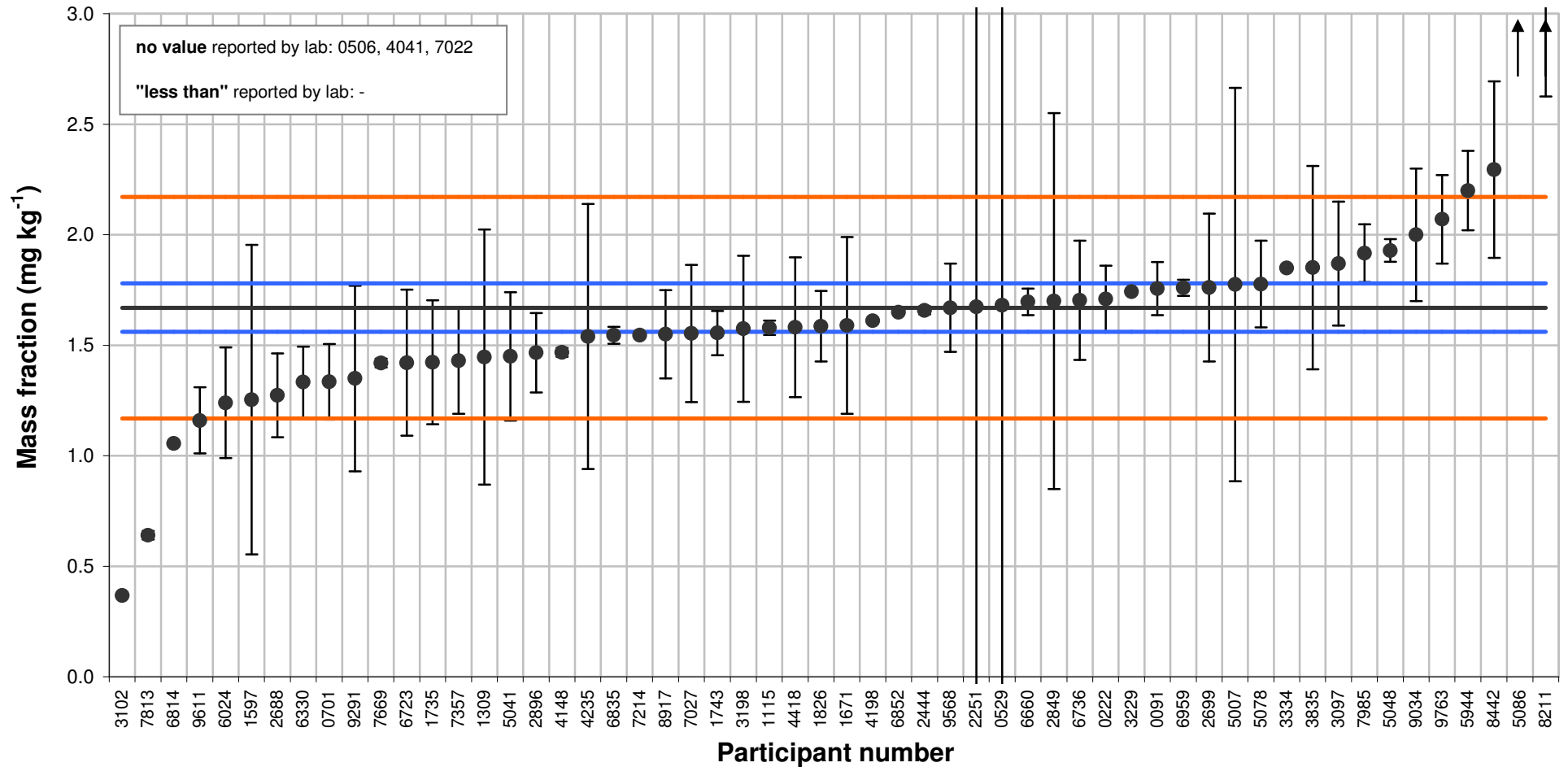
^a √3 is set by the ILC coordinator when no expansion factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with $k=√3$. For explanation see Ch 9.3

^b Satisfactory, Questionable, Unsatisfactory

^c Where: **a** : $u_{min} \leq u_{lab} \leq u_{max}$, **b** : $u_{lab} < u_{min}$, and **c** : $u_{lab} > u_{max}$

IMEP-29 (Heavy metals in feed of plant origin): Total Lead

Certified value: $X_{\text{ref}} = 1.67 \text{ mg} \cdot \text{kg}^{-1}$; $U_{\text{ref}} = 0.11 \text{ mg} \cdot \text{kg}^{-1}$ ($k=2$)



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.

The thick black line corresponds to X_{ref} , the blue lines mark the boundary of the reference interval ($X_{\text{ref}} \pm 2u_{\text{ref}}$), and the orange lines that of the target interval ($X_{\text{ref}} \pm 2\sigma$).

Annex 11 : Results for Extractable Lead

$X_{ref} = 1.67$ and $U_{ref} = 0.11$; all values are given in (mg kg⁻¹)

Part Nr	x1	x2	x3	x4	U _{lab}	k ^a	Mean (x _{lab})	u _{lab}	Technique	z ^b	ζ ^b	Unc ^c
0529	1.50	1.70	1.58		10	√3	1.593	6	ETAAS	-0.3	0.0	c
1115	1.565	1.549	1.497		0.088	√3	1.537	0.051	ICP-MS	-0.5	-1.8	b
1309	1.31	1.76			0.61	2	1.54	0.31	ETAAS	-0.5	-0.4	c
1597	1.139	1.505	1.118		0.7	2	1.3	0.4	ETAAS	-1.7	-1.2	c
1671	1.76	1.71	1.83		0.44	2	1.77	0.22	ICP-MS	0.4	0.4	a
1735	0.149	0.144	0.146		0.029	√3	0.146	0.017	ICP-AES	-6.1	-26.5	b
1743	1.496	1.546	1.474		0.12	√3	1.5	0.07	ICP-MS	-0.7	-1.9	a
1826	1.63	1.64	1.64		0.164	2	1.64	0.082	ICP-MS	-0.1	-0.3	a
2444	1.651	1.579			0.047	2	1.615	0.024	ICP-MS	-0.2	-0.9	b
2699	1.258	1.230	1.366		0.244	√3	1.285	0.141	FAAS	-1.5	-2.5	a
2849	1.59	1.62	1.64		0.80	√3	1.62	0.46	ICP-MS	-0.2	-0.1	c
2896	1.34	1.38	1.41		0.32	2	1.38	0.16	ICP-MS	-1.2	-1.7	a
3097	1.655	1.596			0.244	2	1.626	0.122	ICP-MS	-0.2	-0.3	a
3835	1.78	1.832	1.766		0.45	2	1.793	0.23	ETAAS	0.5	0.5	a
4198	1.260	1.244			0.001	2	1.252	0.001	Graphite-furnace AAS	-1.7	-7.6	b
4235	1.512	1.486			0.579	2	1.499	0.290	ICP-MS	-0.7	-0.6	c
5007	1.781	1.779	1.790		0.89	2	1.783	0.45	ICP-MS	0.5	0.3	c
5041	1.44	1.37			0.28	2	1.41	0.14	HR-ICP-MS	-1.1	-1.8	a
5078	2.06	1.89	1.99		0.218	2	1.98	0.109		1.2	2.5	a
5086	2.95	3.04			0.15	√3	3.00	0.09	FAAS	5.3	12.9	a
5944	1.7	2.0			0.34	√3	1.9	0.20	ETAAS	0.7	0.9	a
6330	0.405	0.438	0.479	0.440	0.053	2	0.441	0.027	ETAAS	-4.9	-20.1	b
6660	1.73	1.74	1.69		0.07	2	1.72	0.04	ICP-MS	0.2	0.8	b
6723	1.148				0.269	2	1.148	0.135	FAAS	-2.1	-3.6	a
6736	1.41	1.38	1.30		0.12	2.48	1.36	0.05	ICP-AES	-1.2	-4.2	b
6835	1.51	1.75	1.73	1.660	0.133	1	1.663	0.133	ICP-MS	0.0	-0.1	a
6852				1.65	0	√3	1.65	0	ICP-MS	-0.1	-0.4	b
7669	1.4249	1.4398			0.0254	2	1.4324	0.0127	ICP-MS	-0.9	-4.2	b
7813	0.59	0.59	0.58	0.60	0.02	2	0.59	0.01	AAS furnace technique	-4.3	-19.3	b
7985	1.96	1.87	2.00		0.13	2	1.94	0.07	ICP-MS	1.1	3.2	a
8211	2.911	3.162	3.277		0.779	2	3.117	0.390	HGA-AAS (furnace oven)	5.8	3.7	c
8442	2.03	2.01	2.03	2.02	0	√3	2.02	0	ETAAS	1.4	6.4	b
8917	1.47	1.47	1.48		0.19	2	1.47	0.10	ICP-MS	-0.8	-1.8	a
9034	2.5	2.7	2.9		0.7	2	2.7	0.4	ETAAS	4.1	2.9	c
9291	1.5	1.5			0.45	2	1.5	0.23	ETAAS	-0.7	-0.7	a
9611	0.134	0.155	0.135	0.134	0.015	100	0.140	0.000	ETAAS	-6.1	-27.8	b
9763	2.67	2.56	2.69		0.14	2	2.64	0.07	FAAS	3.9	10.9	a

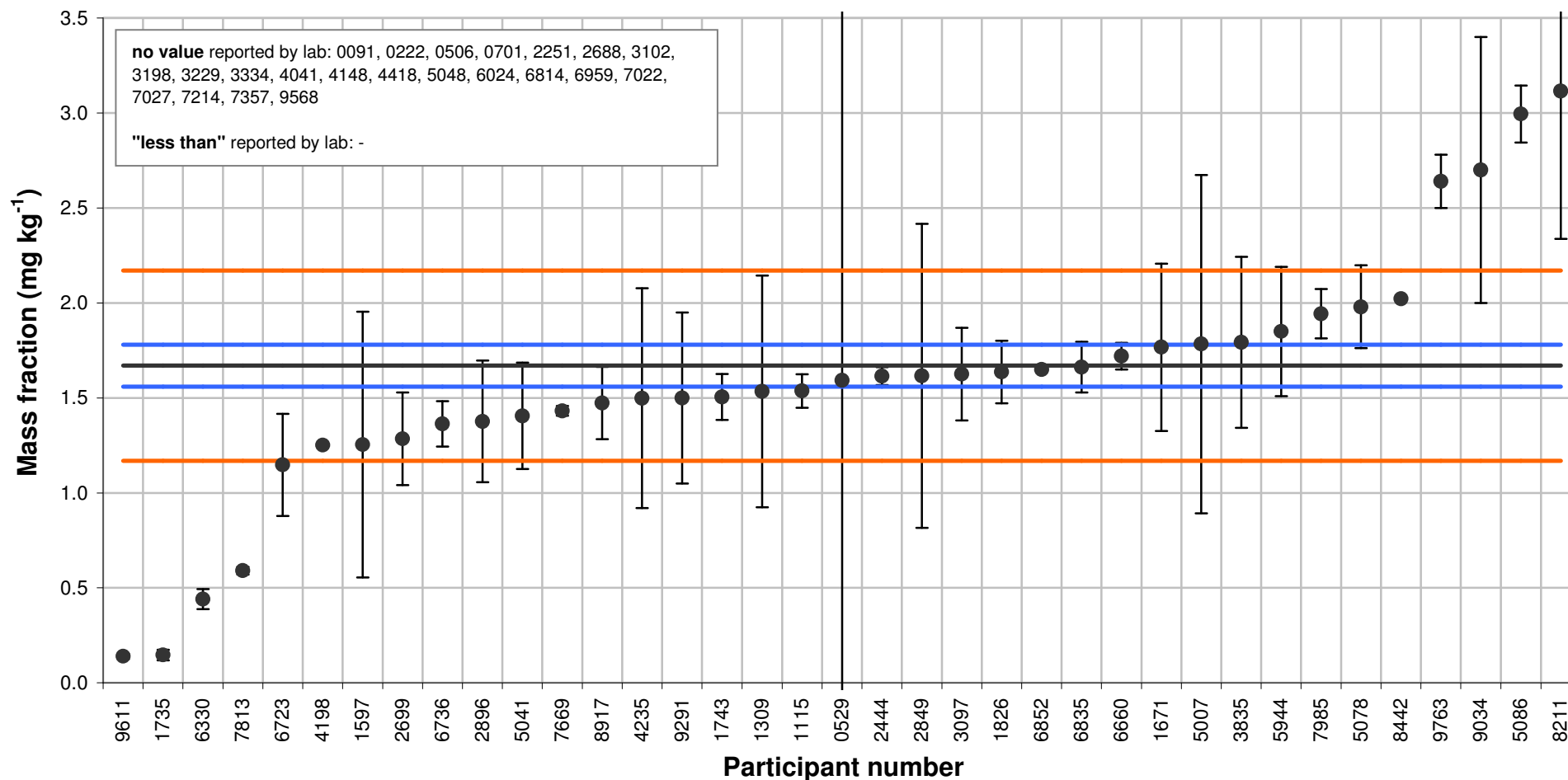
^a √3 is set by the ILC coordinator when no expansion factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with $k=√3$. For explanation see Ch 9.3

^b Satisfactory, Questionable, Unsatisfactory

^c Where: **a** : $U_{min} \leq U_{lab} \leq U_{max}$, **b** : $U_{lab} < U_{min}$, and **c** : $U_{lab} > U_{max}$

IMEP-29 (Heavy metals in feed of plant origin): Extractable Lead

Certified value: $X_{\text{ref}} = 1.67 \text{ mg} \cdot \text{kg}^{-1}$; $U_{\text{ref}} = 0.11 \text{ mg} \cdot \text{kg}^{-1}$ ($k=2$)



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.

The thick black line corresponds to X_{ref} , the blue lines mark the boundary of the reference interval ($X_{\text{ref}} \pm 2U_{\text{ref}}$), and the orange lines that of the target interval ($X_{\text{ref}} \pm 2\sigma$).

Annex 12 : Results for Total Arsenic

X_{ref} = 0.042 and U_{ref} = 0.010; all values are given in (mg kg⁻¹)

Part Nr	x1	x2	x3	x4	U _{lab}	k ^a	Mean (x _{lab})	u _{lab}	Technique	z ^b	ζ ^b	Unc ^c
0091	<0.20	<0.25	<0.24	<0.25					k0-INAA (k0-Instrumental Neutron Activation Analysis)			
0222	0.140	0.112	0.129		0.020	2	0.127	0.010	ICP-DRC-MS	13.5	7.6	c
0506	0.038	0.035	0.036		0.004	2	0.036	0.002	HG-AAS	-0.9	-1.1	b
0529	<0.05	<0.05	<0.05	<0.05					ETAAS			
0701	0.0378	0.0383	0.0380		0.0079	1.06	0.0380	0.0075	HG-AAS	-0.6	-0.4	c
1115	0.036	0.033	0.035	0.034	0.0027	√3	0.035	0.0016	ICP-MS	-1.2	-1.4	b
1309	0.071	0.060	0.060		0.006	2	0.064	0.003	HG-AAS	3.4	3.7	b
1597	0.618	0.611	0.630	0.61	0.18	2	0.62	0.09	ICP-MS	91.3	6.4	c
1671	0.058	0.049	0.066	0.057	0.029	2	0.058	0.015	HG-AAS	2.5	1.0	c
1735	0.052	0.052			0.010	2	0.052	0.005	CV-AFS	1.6	1.4	a
1743	0.052	0.058	0.051	0.053	0.013	√3	0.054	0.008	ICP-MS	1.8	1.3	c
1826	0.038	0.036	0.034		0.0036	2	0.036	0.0018	ICP-MS	-1.0	-1.1	b
2251	0.0623	0.0675	0.0620		23	2	0.0639	12	ICP-MS	3.5	0.0	c
2444	0.000	0.095			0.068	√3	0.048	0.039	ICP-MS	0.9	0.1	c
2688	<0.5	<0.5	<0.5	<0.5					ICP-AES			
2849	<0.03	<0.03	<0.03	<0.03					ICP-MS			
2896	0.0301	0.0342	0.0311		0.0054	2	0.0318	0.0027	ICP-MS	-1.6	-1.8	b
3097	0.058	0.063	0.058		0.008	2	0.060	0.004	ICP-MS	2.8	2.8	b
3102	<0.12	<0.12	<0.12	<0.12					ETAAS			
3229	0.05	0.06	0.04		0	√3	0.05	0	HG-AAS	1.3	1.6	b
3334	0.52	0.56			0	√3	0.54	0	HG-AAS	79.0	99.6	b
3835	0.040	0.038	0.037		0.019	2	0.038	0.010	HG-AAS	-0.6	-0.3	c
4148	0.022	0.020			0.013	√3	0.021	0.008	HG-AAS	-3.3	-2.3	c
4198	0.036	0.024			0.007	2	0.030	0.004	HG-AAS	-1.9	-2.0	b
4235	0.038	0.034			0.005	2	0.036	0.003	ICP-MS	-1.0	-1.1	b
4418	0.124				0.025	2	0.124	0.013	ICP-AES	13.0	6.1	c
5007	0.041	0.036	0.046		0.021	2	0.041	0.011	HG-AAS	-0.2	-0.1	c
5041	<0.2	<0.2							HR-ICP-MS			
5078	0.037	0.033	0.037		0.003	2	0.036	0.002	HG-AAS	-1.0	-1.2	b
6024	0.064	0.069	0.066		0.020	2	0.066	0.010	HG-AAS	3.9	2.2	c
6330	0.041	0.036	0.035		0.005	2	0.037	0.003	HG-AAS	-0.7	-0.8	b
6660	0.0359	0.0357	0.0380		0.0032	2	0.0365	0.0016	HG-AAS	-0.9	-1.0	b
6723	<0.15											
6736	0.263	0.236	0.202	0.233	0.077	2.48	0.234	0.031	ICP-MS	30.4	6.1	c
6814	<0.5	<0.5	<0.5	<0.5					ICP-AES			
6835	0.022	0.020	0.018		0.0015	1	0.020	0.0015	ICP-MS	-3.5	-4.2	b
6852				0.053	0	√3	0.053	0	ICP-MS	1.7	2.2	b
6959	0.025	0.023	0.029		0.004	2	0.026	0.002	ICP-MS	-2.6	-3.0	b
7214	0.03	0.02			0	√3	0.03	0	CV-AFS	-2.7	-3.4	b
7357	0.034	0.031	0.030	0.031	0.003	2	0.032	0.002	ICP-MS	-1.7	-2.0	b
7669	0.0598	0.0603	0.0623		0.0024	2	0.0608	0.0012	ICP-MS	3.0	3.7	b
7813	<0.5	<0.5	<0.5	<0.5					AAS furnace technique			
7985	0.059	0.056	0.064		0.009	2	0.060	0.005	ICP-MS	2.8	2.6	b
8211	0.691	0.432	0.910	0.677	0.183	2	0.678	0.092	HGA-AAS (furnace oven)	100.9	6.9	c
8917	0.034	0.038	0.036		0.008	2	0.036	0.004	ICP-MS	-1.0	-0.9	b
9291	0.037	0.042			0.012	2	0.040	0.006	HG-AAS	-0.4	-0.3	a
9568	0.032	0.031	0.031		0.004	√3	0.0313	0.002	HG-AAS	-1.7	-1.9	b
9611	0.122	0.141	0.122	0.134	0.021	100	0.12975	0.000	ETAAS	13.9	17.5	b
9763	<0.01	<0.01	<0.01	<0.01					HG-AAS			

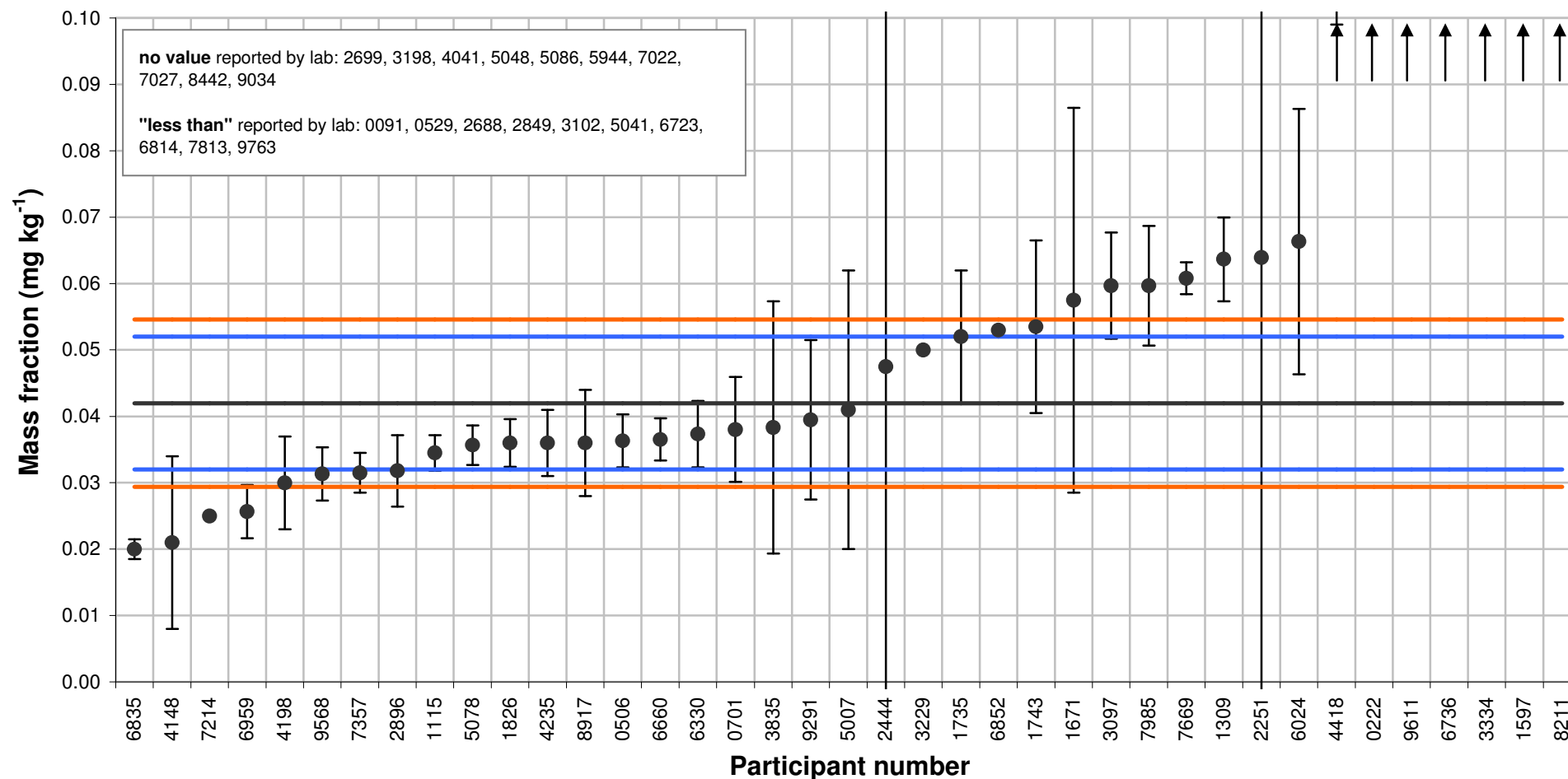
^a √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

^b Satisfactory, Questionable, Unsatisfactory

^c Where: **a** = U_{min} ≤ U_{lab} ≤ U_{max}, **b** : U_{lab} < U_{min}, and **c** : U_{lab} > U_{max}

IMEP-29 (Heavy metals in feed of plant origin): Total Arsenic

Certified value: $X_{\text{ref}} = 0.042 \text{ mg} \cdot \text{kg}^{-1}$; $U_{\text{ref}} = 0.01 \text{ mg} \cdot \text{kg}^{-1}$ ($k=2$)



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.

The thick black line corresponds to X_{ref} , the blue lines mark the boundary of the reference interval ($X_{\text{ref}} \pm 2U_{\text{ref}}$), and the orange lines that of the target interval ($X_{\text{ref}} \pm 2\sigma$).

Annex 13 : Results for Total Mercury

X_{ref} = 0.0164 and U_{ref} = 0.0022; all values are given in (mg kg⁻¹)

Part Nr	x1	x2	x3	x4	U _{lab}	k ^a	Mean (x _{lab})	u _{lab}	Technique	z ^b	ζ ^b	Unc ^c
0091	0.0131	0.0125	0.0132		0.0009	1	0.0129	0.0009	CV-AAS	-1.4	-2.4	b
0222	0.023				0.005	2	0.023	0.003	ICP-MS	2.7	2.4	c
0506	0.0215	0.0219	0.0231		0.0031	2	0.0222	0.0016	ETAAS	2.3	3.0	a
0529	0.0162	0.0181	0.0173		10	√3	0.0172	6	AAS-AMA 254	0.3	0.0	c
0701	0.016	0.017	0.016		0.002	1.07	0.016	0.002	CV-AAS	0.0	0.0	a
1115	0.029	0.035	0.030		0.0056	√3	0.031	0.0032	CV-AAS	6.1	4.4	c
1309	0.020	0.019	0.019		0.005	2	0.019	0.003	CV-AAS	1.2	1.1	c
1597	0.014	0.014	0.014		0.02	2	0.014	0.01	AMA	-1.0	-0.2	c
1671	0.020	0.017	0.018		0.009	2	0.018	0.005	CV-AAS	0.8	0.4	c
1735	0.018	0.017	0.018		0.002	2	0.018	0.001	AAS-DMA	0.5	0.9	b
1743	0.036	0.026	0.035		0.019	√3	0.032	0.011	CV-AAS	6.5	1.4	c
1826	0.018	0.017	0.016		0.0034	2	0.017	0.0017	ICP-MS	0.2	0.3	a
2688	<0.3	<0.3	<0.3	<0.3					ICP-AES			
2699	0.058	0.065	0.057		0.003	√3	0.060	0.002	CV-AAS	17.7	21.2	a
2849	0.014	0.014	0.016		0.007	√3	0.015	0.004	CV-AAS	-0.7	-0.4	c
2896	0.0172	0.0168	0.0171		0.0039	2	0.0170	0.0020	CV-AFS	0.3	0.3	a
3097	0.015	0.016	0.015		0.003	2	0.015	0.002	AMA	-0.4	-0.6	a
3102	0.069	0.066	0.069		0	√3	0.068	0	HG-AAS	21.0	46.9	b
3198	0.0150	0.0148	0.0143		0.0049	2	0.0147	0.0025	DMA 80	-0.7	-0.6	a
3229	0.018	0.017	0.017	0.018	0	√3	0.018	0	CV-AAS	0.4	1.0	b
3835	0.0167	0.0159	0.0160		0.0081	2	0.0162	0.0041	CV-AAS	-0.1	0.0	c
4041	0.017	0.016	0.016		0.003	2	0.016	0.002	AMA 254	0.0	0.0	a
4148	0.020	0.021	0.021	0.020	0.001	√3	0.021	0.001	HG-AAS	1.7	3.3	b
4198	0.022	0.021			0.007	2	0.022	0.004	AMA254-technique	2.1	1.4	c
4235	0.015	0.014			0.003	2	0.015	0.002	ICP-MS	-0.8	-1.0	a
4418	0.362				0.072	√3	0.362	0.042	ICP-AES	140.5	8.3	c
5007	0.019	0.022	0.025		0.009	2	0.022	0.005	CV-AAS	2.3	1.2	c
5041	0.0175	0.0201			0	√3	0.0188	0	HR-ICP-MS	1.0	2.2	b
5078	0.022	0.034	0.015		0.005	2	0.024	0.003	CV-AAS	3.0	2.7	c
5944	0.02	0.02			0.0004	√3	0.02	0.0002	CV-AAS	1.5	3.2	b
6024	<0.02	<0.02	<0.02						CV-AAS			
6330	0.0172	0.0170	0.0181		0.0028	2	0.0174	0.0014	AMA 254	0.4	0.6	a
6660	0.0166	0.0169	0.0164		0.0006	2	0.0166	0.0003	CV-AAS	0.1	0.2	b
6723	0.0105	0.01117	0.0103		0.0024	2	0.01066	0.0012	AMA 254	-2.3	-3.5	a
6736				<0.07								
6814	<0.1	<0.1	<0.1	<0.1					CV-AAS			
6835	0.011	0.011	0.011	0.012	0.0012	1	0.011	0.0012	CV-AFS	-2.1	-3.2	a
6959	0.020	0.021	0.023		0.002	2	0.021	0.001	ICP-MS	2.0	3.3	b
7214	0.017	0.017			0	√3	0.017	0	Direct Analysis (Amalgam)	0.2	0.5	b
7357	0.024	0.027	0.024		0.003	2	0.025	0.002	Mercury analyzer, cold vapour	3.5	4.6	a
7669	0.0214	0.0217			0	√3	0.0216	0	ICP-MS	2.1	4.7	b
7813	0.19	0.18	0.19		0.04	2	0.19	0.02	CV-AAS	69.2	8.5	c
7985	<0.05	<0.05	<0.05	<0.05					ICP-MS			
8211	<0.019	<0.019	<0.019	<0.019					CV-AAS			
8442	0.08	0.07	0.09		0.04	2	0.08	0.02	HG-AAS	25.9	3.2	c
8917	0.021	0.022	0.022	0.021	0.004	2	0.022	0.002	ICP-MS	2.1	2.2	a
9034	0.032	0.034	0.034		0.003	2	0.033	0.002	CV-AAS	6.9	9.1	a
9291	0.019	0.018			0.004	2	0.019	0.002	TDA-AAS	0.9	0.9	a
9568	0.0173	0.0171	0.0178		0.002	√3	0.0174	0.001	CV-AAS	0.4	0.6	a
9611	0.0157	0.0165	0.0161		0.0013	100	0.016	0.0000	AMA 254	-0.1	-0.3	b
9763	0.099	0.093	0.099	0.096	0.007	2	0.097	0.004	CV-AAS	32.7	21.9	c

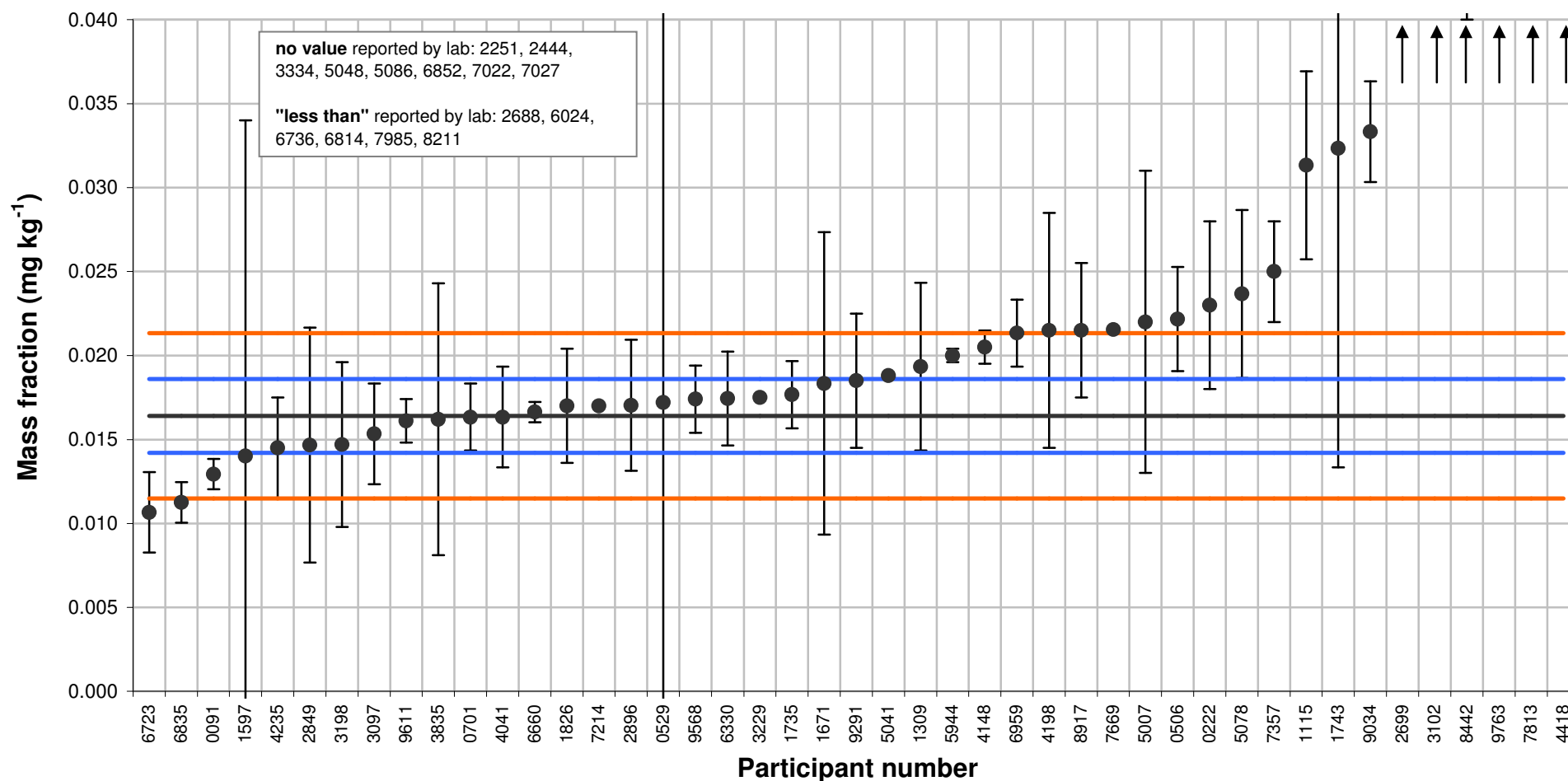
^a √3 is set by the ILC coordinator when no expansion factor k is reported. The reported uncertainty was assumed to have a rectangular distribution with $k=\sqrt{3}$. For explanation see Ch 9.3

^b Satisfactory, Questionable, Unsatisfactory

^c Where: **a** = $U_{\min} \leq U_{\text{lab}} \leq U_{\max}$, **b** : $U_{\text{lab}} < U_{\min}$, and **c** : $U_{\text{lab}} > U_{\max}$

IMEP-29 (Heavy metals in feed of plant origin): Total Mercury

Certified value: $X_{\text{ref}} = 0.0164 \text{ mg} \cdot \text{kg}^{-1}$; $U_{\text{ref}} = 0.0022 \text{ mg} \cdot \text{kg}^{-1}$ ($k=2$)



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.

The thick black line corresponds to X_{ref} , the blue lines mark the boundary of the reference interval ($X_{\text{ref}} \pm 2U_{\text{ref}}$), and the orange lines that of the target interval ($X_{\text{ref}} \pm 2\sigma$).

Annex 14 : Results for Total Tin

X_{ref} = 0.062 and U_{ref} = 0.011; all values are given in (mg kg⁻¹)

Part Nr	x1	x2	x3	x4	U _{lab}	k ^a	Mean (x _{lab})	u _{lab}	Technique	z ^b	ζ ^b	Unc ^c
0091	<6	<6	<5	<6					k0-INAA (k0-Instrumental Neutron Activation Analysis)			
0222	0.061	0.059	0.064		0.005	2	0.061	0.003	ICP-MS	-0.1	-0.1	b
0506	<25.8	<25.8	<25.8						FAAS			
0529	0.21	0.24	0.24	0.22	12	√3	0.23	7	ETAAS	17.8	0.0	c
1115	0.064	0.066	0.071		0.038	√3	0.067	0.022	ICP-MS	0.5	0.2	c
1671	0.055	0.057			0.028	2	0.056	0.014	ICP-MS	-0.6	-0.4	c
1735	18.0	16.9	17.3		1.74	2	17.4	0.87	ICP-AES	1864.3	19.9	c
1743	<0.1	<0.1	<0.1	<0.1					ICP-MS			
1826	0.043	0.046	0.070		0.033	2	0.053	0.017	ICP-MS	-1.0	-0.5	c
2251	0.0465	0.0473	0.0463		50	2	0.0467	25	ICP-MS	-1.6	0.0	c
2688	<1	<1	<1	<1					ICP-AES			
3097	0.047	0.041	0.047		0.009	2	0.045	0.005	ICP-MS	-1.8	-2.4	b
3198	<0.3	<0.3	<0.3	<0.3					ETAAS			
3835	0.058	0.067	0.062		0.0155	2	0.062	0.0078	ICP-MS	0.0	0.0	a
4198	<0.2	<0.2							ICP-MS			
4235	0.038	0.037			0.003	2	0.038	0.002	ICP-MS	-2.6	-4.3	b
5041	<0.2	<0.2							HR-ICP-MS			
6024	<4	<4	<4	<4					FAAS			
6660	0.0713	0.0795	0.0747		0.010	2	0.0752	0.005	ICP-MS	1.4	1.8	b
6723	21.5				5.5	2	21.5	2.8	FAAS	2305.2	7.8	c
6814	17.55	16.15	15.16		0	√3	16.29	0	ICP-AES	1744.6	2949.9	b
6835	0.042	0.045	0.043	0.044	0.0012	1	0.044	0.0012	ICP-MS	-2.0	-3.3	b
6852	0.070				0	√3	0.07	0	ICP-MS	0.9	1.5	b
6959	0.061	0.063	0.065		0.004	2	0.063	0.002	ICP-MS	0.1	0.2	b
7027	126.0	128.0	130.0		5.12	2	128.0	2.56	FAAS	13756.8	50.0	c
7669	0	0	0	0					ICP-AES			
8917	0.057	0.054	0.053	0.054	0.004	2	0.055	0.002	ICP-MS	-0.8	-1.3	b

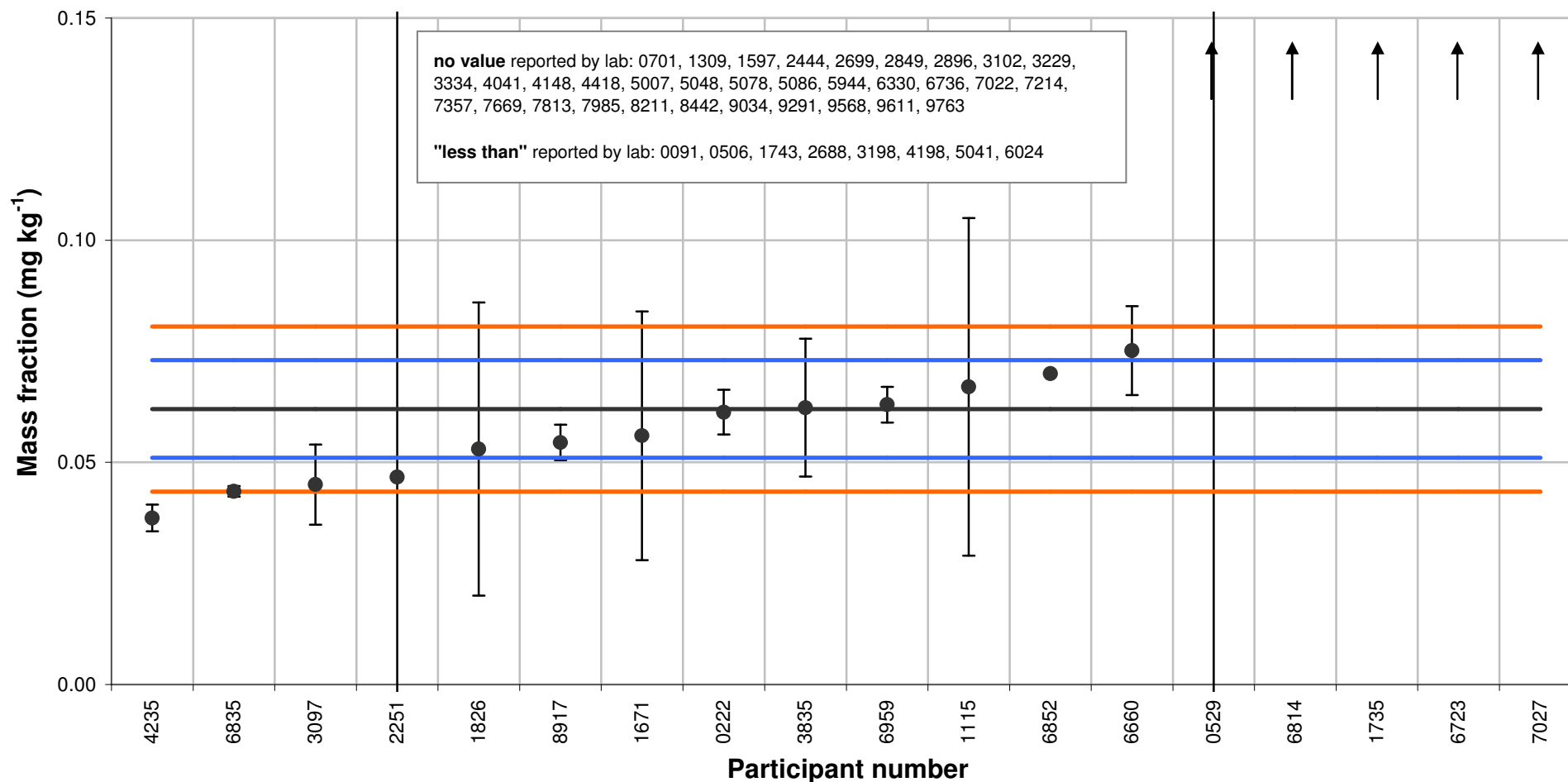
^a √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3

^b **Satisfactory**, **Questionable**, **Unsatisfactory**

^c Where: **a** = U_{min} ≤ U_{lab} ≤ U_{max}, **b** : U_{lab} < U_{min} , and **c** : U_{lab} > U_{max}

IMEP-29 (Heavy metals in feed of plant origin): Total Tin

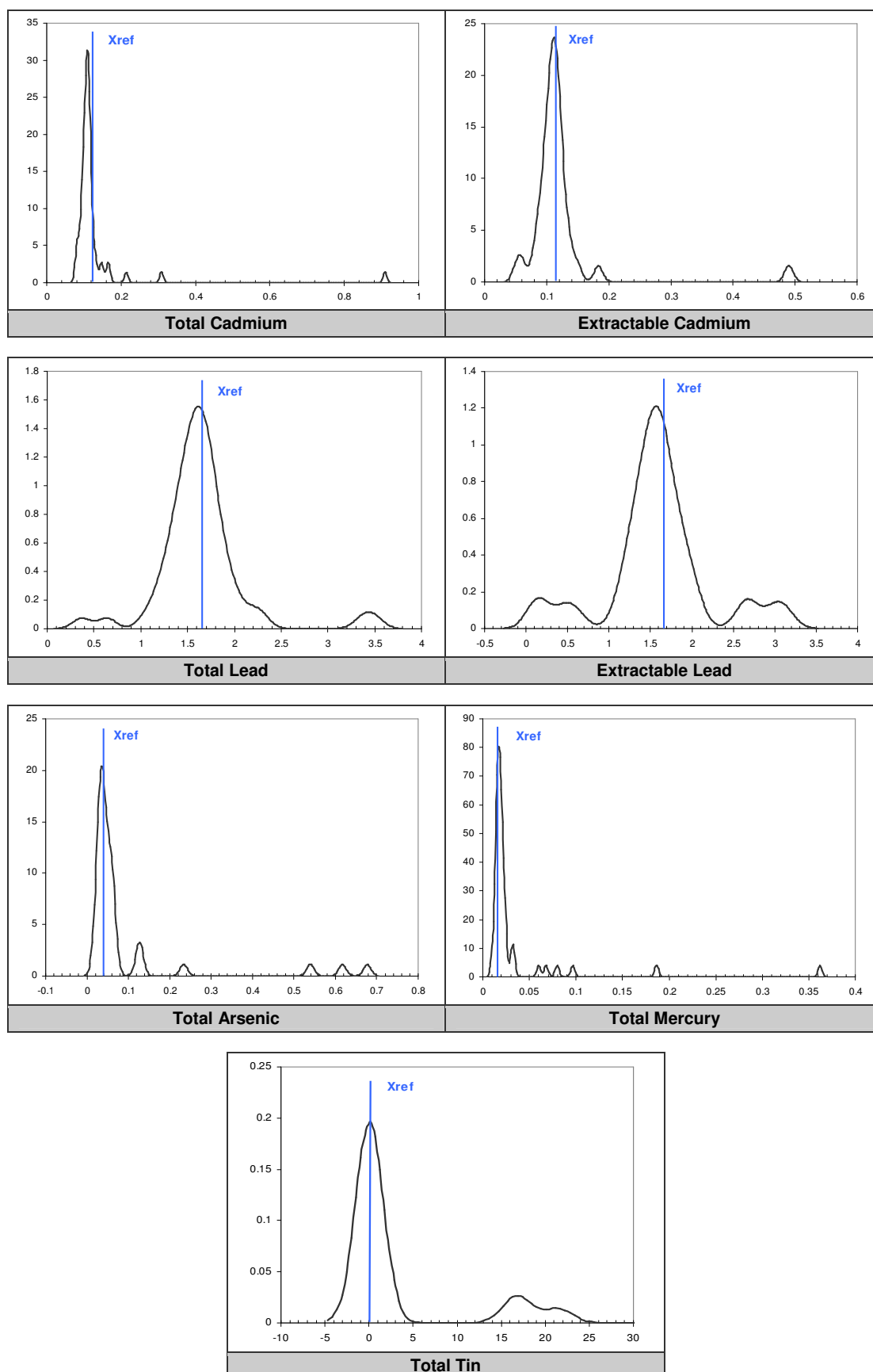
Certified value: $X_{\text{ref}} = 0.062 \text{ mg} \cdot \text{kg}^{-1}$; $U_{\text{ref}} = 0.011 \text{ mg} \cdot \text{kg}^{-1}$ ($k=2$)



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.

The thick black line corresponds to X_{ref} , the blue lines mark the boundary of the reference interval ($X_{\text{ref}} \pm 2U_{\text{ref}}$), and the orange lines that of the target interval ($X_{\text{ref}} \pm 2\sigma$).

Annex 15 : Kernel densities [mg kg⁻¹]



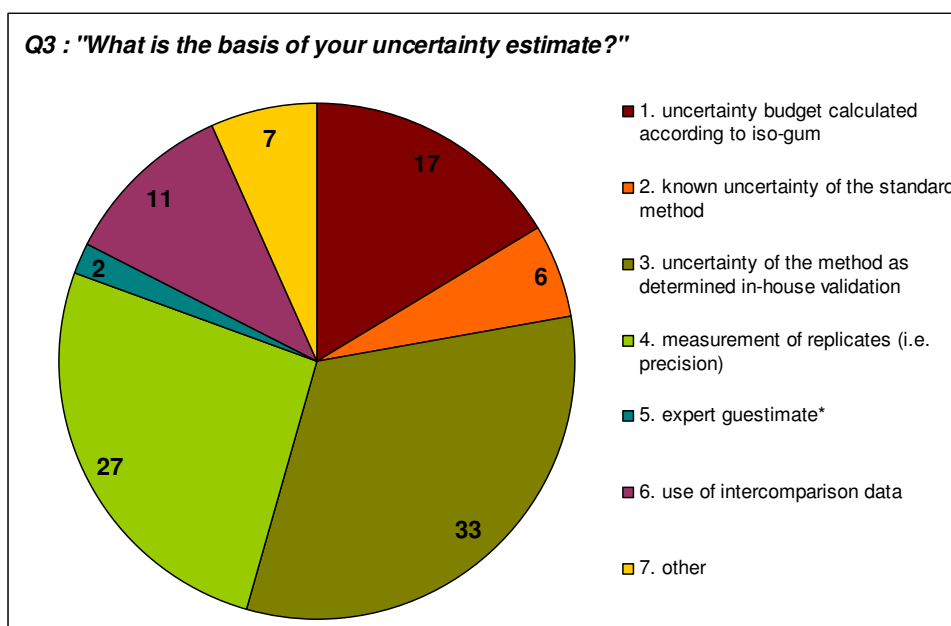
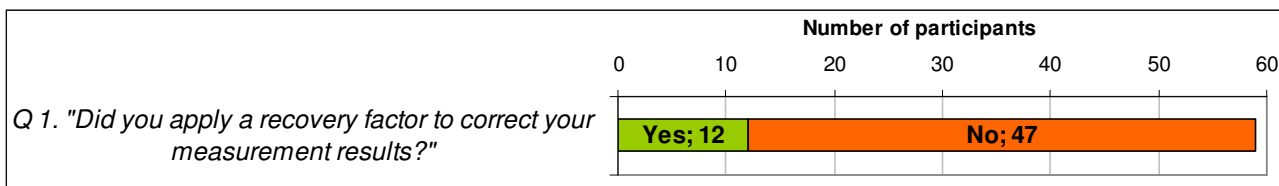
Annex 16 : Summary of scorings

Part Nr	Total Cd			Extractable Cd			Total Pb			Extractable Pb			Total As			Total Hg			Total Tin		
	z [†]	z [†]	Unc [‡]	z [†]	z [†]	Unc [‡]	z [†]	z [†]	Unc [‡]	z [†]	z [†]	Unc [‡]	z [†]	z [†]	Unc [‡]	z [†]	z [†]	Unc [‡]	z [†]	z [†]	Unc [‡]
0091	-0.3	-0.9	a				0.3	0.7	a							-1.4	-2.4	b			
0222	-0.2	-0.8	a				0.2	0.4	a				13.5	7.6	c	2.7	2.4	c	-0.1	-0.1	b
0506													-0.9	-1.1	b	2.3	3.0	a			
0529	-0.6	0.0	c	-3.1	0.0	c	0.0	0.0	c	-0.3	0.0	c				0.3	0.0	c	17.8	0.0	c
0701	2.5	2.8	a				-1.3	-2.0	a				-0.6	-0.4	c	0.0	0.0	a			
1115	-0.7	-2.6	b	-0.5	-1.7	a	-0.4	-1.6	b	-0.5	-1.8	b	-1.2	-1.4	b	6.1	4.4	c	0.5	0.2	c
1309	-1.5	-0.9	c	-2.0	-1.3	c	-0.9	-0.8	c	-0.5	-0.4	c	3.4	3.7	b	1.2	1.1	c			
1597							-1.7	-1.2	c	-1.7	-1.2	c	91.3	6.4	c	-1.0	-0.2	c			
1671	-0.4	-0.5	a	0.5	0.6	a	-0.3	-0.4	a	0.4	0.4	a	2.5	1.0	c	0.8	0.4	c	-0.6	-0.4	c
1735	-1.4	-2.7	a	-0.1	-0.1	a	-1.0	-1.6	a	-6.1	-26.5	b	1.6	1.4	a	0.5	0.9	b	1864.3	19.9	c
1743	0.2	0.7	b	0.3	2.5	a	-0.5	-1.4	a	-0.7	-1.9	a	1.8	1.3	c	6.5	1.4	c			
1826	-0.8	-1.7	a	-0.4	-0.9	a	-0.3	-0.9	a	-0.1	-0.3	a	-1.0	-1.1	b	0.2	0.3	a	-1.0	-0.5	c
2251	-0.1	0.0	c				0.0	0.0	c				3.5	0.0	c				-1.6	0.0	c
2444	-0.8	-2.2	a	-0.6	-2.9	a	0.0	-0.2	b	-0.2	-0.9	b	0.9	0.1	c						
2688	-0.9	-1.3	a				-1.6	-3.2	a												
2699	-0.1	-0.2	a	-1.4	-2.8	a	0.4	0.5	a	-1.5	-2.5	a				17.7	21.2	a			
2849	-0.1	-0.1	c	0.1	0.0	c	0.1	0.1	c	-0.2	-0.1	c				-0.7	-0.4	c			
2896	-0.9	-1.0	a	-0.9	-4.0	a	-0.8	-1.9	a	-1.2	-1.7	a	-1.6	-1.8	b	0.3	0.3	a			
3097	0.5	0.8	a	-0.3	-0.5	a	0.8	1.3	a	-0.2	-0.3	a	2.8	2.8	b	-0.4	-0.6	a	-1.8	-2.4	b
3102	-1.1	-5.7	b				-5.2	-23.7	b							21.0	46.9	b			
3198	-1.3	-2.3	a				-0.4	-0.5	a							-0.7	-0.6	a			
3229	-1.1	-5.9	b				0.3	1.3	b				1.3	1.6	b	0.4	1.0	b			
3334	-0.8	-4.3	b				0.7	3.3	b				79.0	99.6	b						
3835	-0.4	-0.2	c	0.2	0.1	c	0.7	0.8	a	0.5	0.5	a	-0.6	-0.3	c	-0.1	0.0	c	0.0	0.0	a
4041																0.0	0.0	a			
4148	-1.3	-6.1	b				-0.8	-3.6	b				-3.3	-2.3	c	1.7	3.3	b			
4198	0.3	1.6	b	-0.1	-1.0	b	-0.2	-1.1	b	-1.7	-7.6	b	-1.9	-2.0	b	2.1	1.4	c			
4235	-0.4	-0.8	a	-0.5	-1.0	a	-0.5	-0.4	c	-0.7	-0.6	c	-1.0	-1.1	b	-0.8	-1.0	a	-2.6	-4.3	b
4418	-0.7	-1.2	a				-0.4	-0.5	a				13.0	6.1	c	140.5	8.3	c			
5007	-0.2	-0.1	c	0.5	0.3	c	0.4	0.2	c	0.5	0.3	c	-0.2	-0.1	c	2.3	1.2	c			
5041	-1.1	-1.9	a	-0.9	-1.5	a	-0.9	-1.4	a	-1.1	-1.8	a				1.0	2.2	b			
5048	10.5	16.4	a				1.0	4.1	b												
5078	-0.5	-1.9	b	0.4	1.8	a	0.4	0.9	a	1.2	2.5	a	-1.0	-1.2	b	3.0	2.7	c			
5086							6.8	12.3	a	5.3	12.9	a									
5944	-0.6	-2.7	b	-1.1	-8.4	a	2.1	4.5	a	0.7	0.9	a				1.5	3.2	b			
6024	-2.1	-4.3	a				-1.7	-3.1	a				3.9	2.2	c						
6330	2.6	5.8	a	-1.3	-5.2	a	-1.3	-3.5	a	-4.9	-20.1	b	-0.7	-0.8	b	0.4	0.6	a			
6660	-0.6	-2.0	a	0.1	0.2	a	0.1	0.4	b	0.2	0.8	b	-0.9	-1.0	b	0.1	0.2	b	1.4	1.8	b
6723	-2.2	-3.7	a	-3.6	-8.1	a	-1.0	-1.4	a	-2.1	-3.6	a				-2.3	-3.5	a	2305.2	7.8	c
6736	-0.6	-1.3	a	-0.6	-2.4	a	0.1	0.3	a	-1.2	-4.2	b	30.4	6.1	c						
6814							-2.5	-11.2	b										1744.6	2949.9	b
6835	-0.7	-2.7	b	0.1	0.1	a	-0.5	-1.9	b	0.0	-0.1	a	-3.5	-4.2	b	-2.1	-3.2	a	-2.0	-3.3	b
6852	-0.7	-3.4	b	1.1	13.1	b	-0.1	-0.4	b	-0.1	-0.4	b	1.7	2.2	b	2.0	3.3	b	0.9	1.5	b
6959	-0.5	-2.3	b				0.4	1.6	b				-2.6	-3.0	b				0.1	0.2	b
7022	1.7	4.9	a	0.9	3.1	a															
7027	-1.5	-2.8	a				-0.5	-0.7	a										13756.8	50.0	c
7214	-1.9	-10.0	b				-0.5	-2.3	b				-2.7	-3.4	b	0.2	0.5	b			
7357	-1.3	-4.3	a				-1.0	-1.8	a				-1.7	-2.0	b	3.5	4.6	a			
7669	-0.9	-4.3	b	0.0	-0.1	a	-1.0	-4.5	b	-0.9	-4.2	b	3.0	3.7	b	2.1	4.7	b			
7813	-0.7	-0.9	a	-1.7	-1.9	a	-4.1	-18.4	b	-4.3	-19.3	b				69.2	8.5	c			
7985	-1.2	-3.3	a	-0.2	-0.5	a	1.0	2.9	a	1.1	3.2	a	2.8	2.6	b						
8211	5.3	4.8	c	4.1	4.2	a	7.3	4.2	c	5.8	3.7	c	100.9	6.9	c						
8442	1.5	1.1	c	2.1	24.8	b	2.5	3.0	a	1.4	6.4	b				25.9	3.2	c			
8917	-0.5	-0.8	a	-0.8	-1.4	a	-0.5	-1.1	a	-0.8	-1.8	a	-1.0	-0.9	b	2.1	2.2	a	-0.8	-1.3	b
9034	-0.4	-0.3	c	1.3	0.8	c	1.3	2.1	a	4.1	2.9	c				6.9	9.1	a			
9291	-0.3	-0.4	a	-0.2	-0.4	a	-1.3	-1.5	a	-0.7	-0.7	a	-0.4	-0.3	a	0.9	0.9	a			
9568	0.8	1.5	a	0.4	0.1	c	0.0	0.0	a				-1.7	-1.9	b	0.4	0.6	a			
9611	-2.2	-11.5	b				-2.0	-9.3	b	-6.1	-27.8	b	13.9	17.5	b	-0.1	-0.3	b			
9763	43.9	129.4	a	22.0	37.2	a	1.6	3.5	a	3.9	10.9	a				32.7	21.9	c			

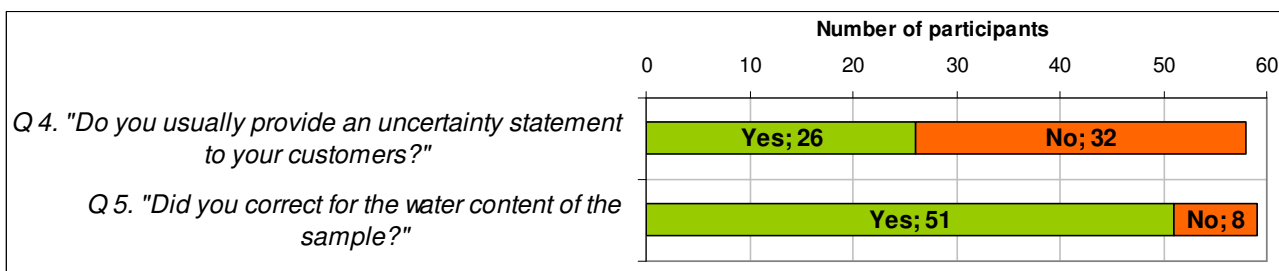
[†] Satisfactory, Questionable, Unsatisfactory

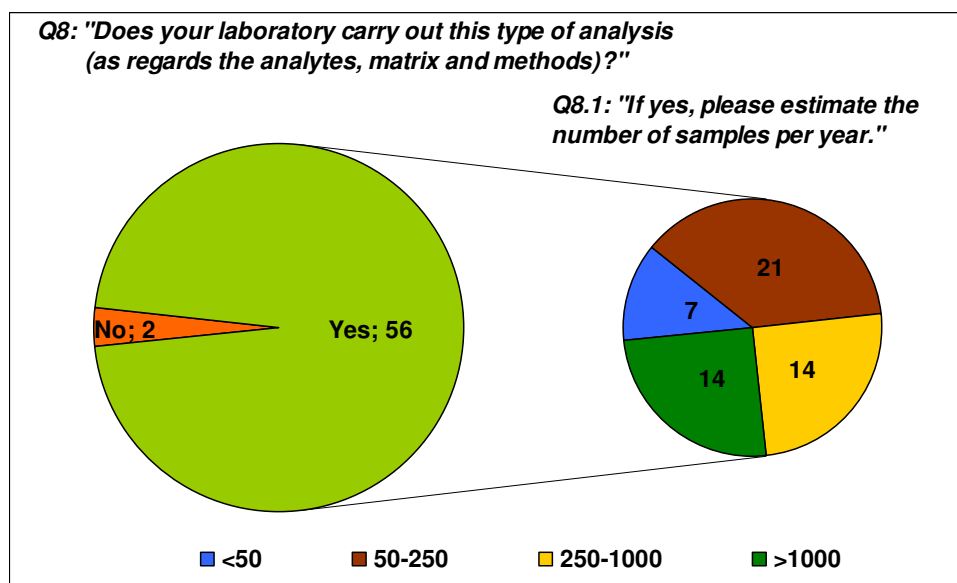
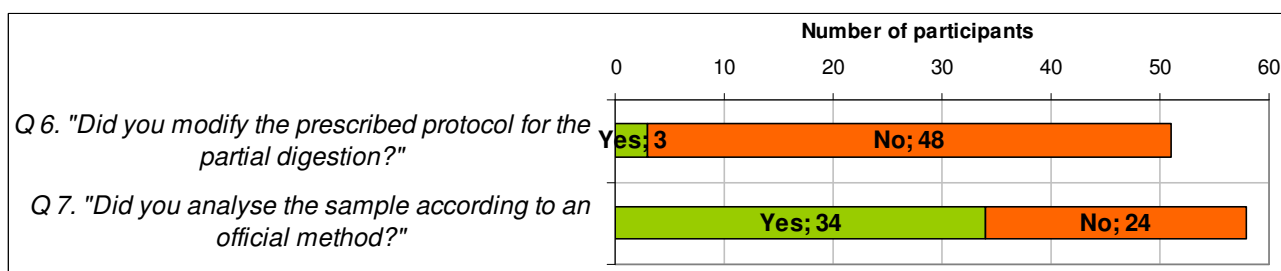
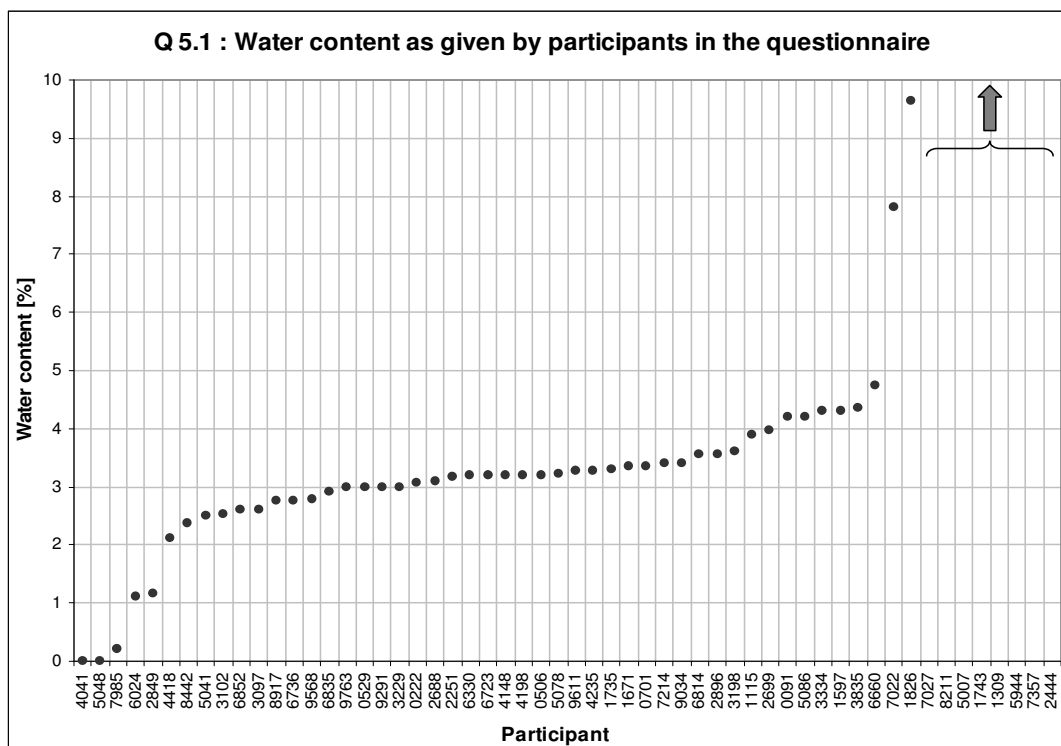
[‡] Where: **a** = U_{min} ≤ U_{lab} ≤ U_{max}, **b** : U_{lab} < U_{min}, and **c** : U_{lab} > U_{max}

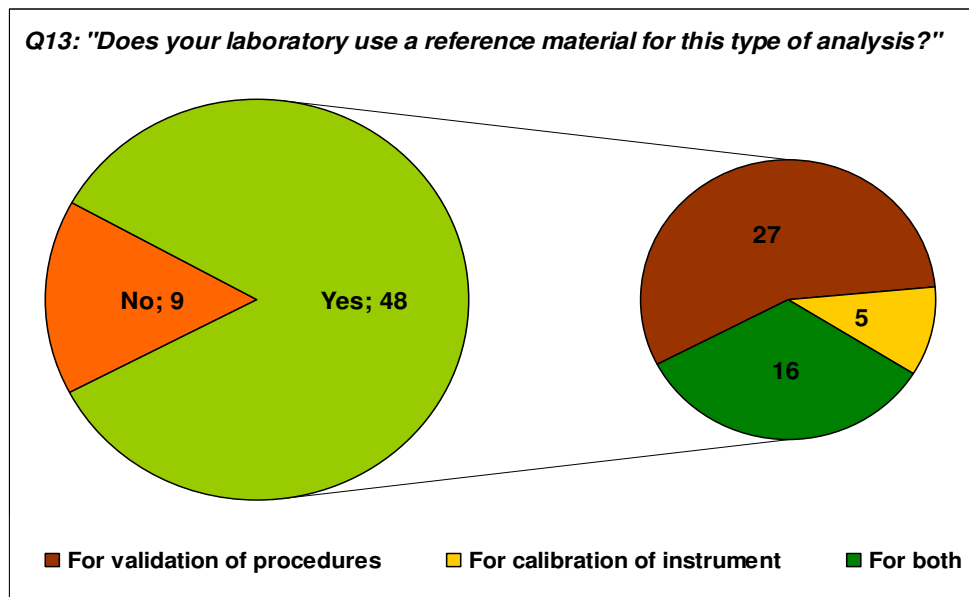
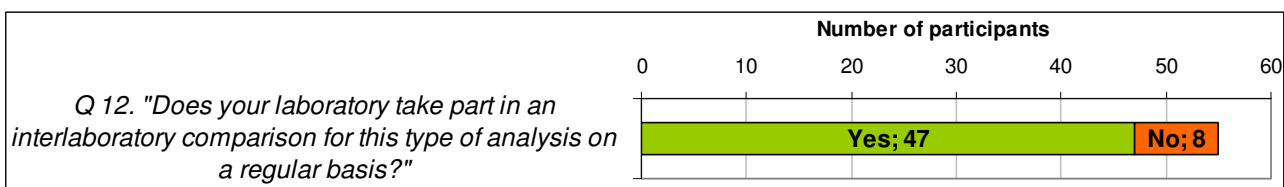
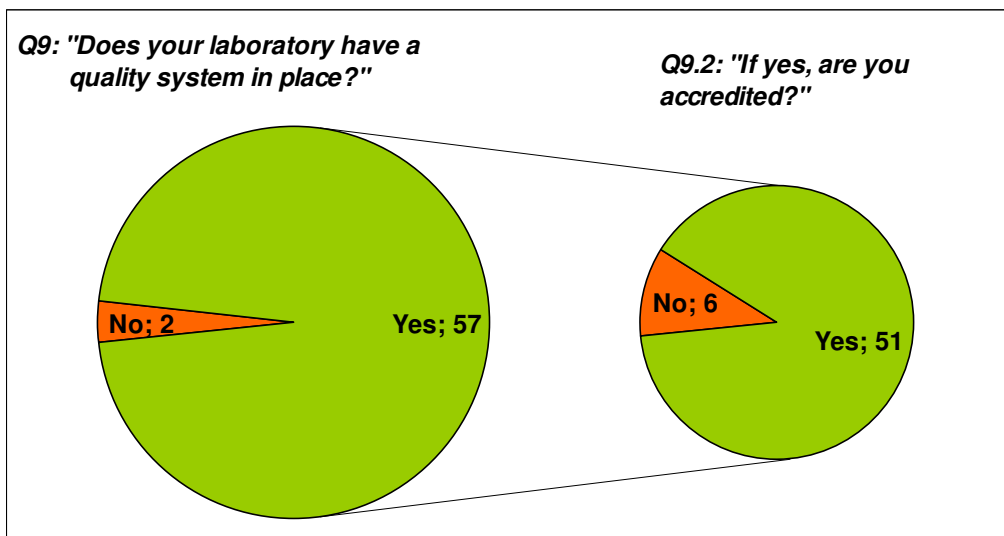
Annex 17 : Evaluation of questionnaire



* expert guesstimate corresponds to "estimation based on judgment", as defined in the Eurachem/CITAC guide on Quantifying Uncertainty in Analytical Measurements







Annex 18 : Experimental details (Q 7.1, Annex 7)

Part Nr	Official Method?	If Yes, which:	If no - sample pre-treatment?	If no - digestion step ?	If no - extraction / separation step ?	If no - instrument calibration ?
0091	no		No	Total digestion, 4 mL of HNO ₃ s.p. and 0.1 mL of HF s.p.	No	For ICP-MS: Multi-elemental stock standard solution for ICP-MS (1000 mg/L). For k0-INAA Al-Au(0.1%) alloy IRMM-530RA
0222	no		Acid digestion in mix (6 ml of Nitric Acid and 2 ml of Hydrogen peroxide) at atmospheric pressure	Mineralization in Acid Solution assisted by MicroWave in closed-teflon vessel. Mineralization cycle is about 60min. The mix is the same used in pre-treatment step.	Not applicable	4 internal standard of appropriate concentration for each element
0506	yes					
0529	yes					
0701	yes					
1115	yes		Homogenisation	microwave 280 °C/80bar, 0,5 g sample, 5 ml HNO ₃ + 1 ml HCl		external standards
1309	no			Hg- AMA 254; Pb,Cd- were digested in muffle furnace; As - were digested in microwave sample preparation system		
1597	yes	extraction conform EN 15510 - measurement AASGF for Pb and Cd	Hg: none ; As: none	Hg: none ; As: microwave digestion	Hg: none ; As: none	Hg: none ; As: external calibration + internal standards for control (no recovery factor)
1671	no		for Pb & Cd: ashing (450 °C)	for Pb & Cd: digestion with hydrochloric acid	for Pb & Cd: filtration	for Pb & Cd: multi point
1735	no					
1743	yes	DIN EN 13805, DIN EN 15763	milling	microwave	microwave	4-point calibration
1826	yes	EN 13805, 2002 and ISO 17294 1+2				
2251	no		Digestion with 5% HNO ₃ and 4% H ₂ O ₂			4 point calibration
2444	no			open wet digestion, Reversed Aqua Regia		
2688	no		dispersion/solubilisation in 65% nitric acid	65% nitric acid, microwave heating, pressurized	none	external calibration
2699	yes	CE 152/2009				
2849	yes	VDLUFA 17.9.1				
2896	yes	VDLUFA MB VII Hg: 2.2.29; As,Pb,Cd: 2.2.2.3				
3097	no		shaking	microwave assisted	nitric acid	yes

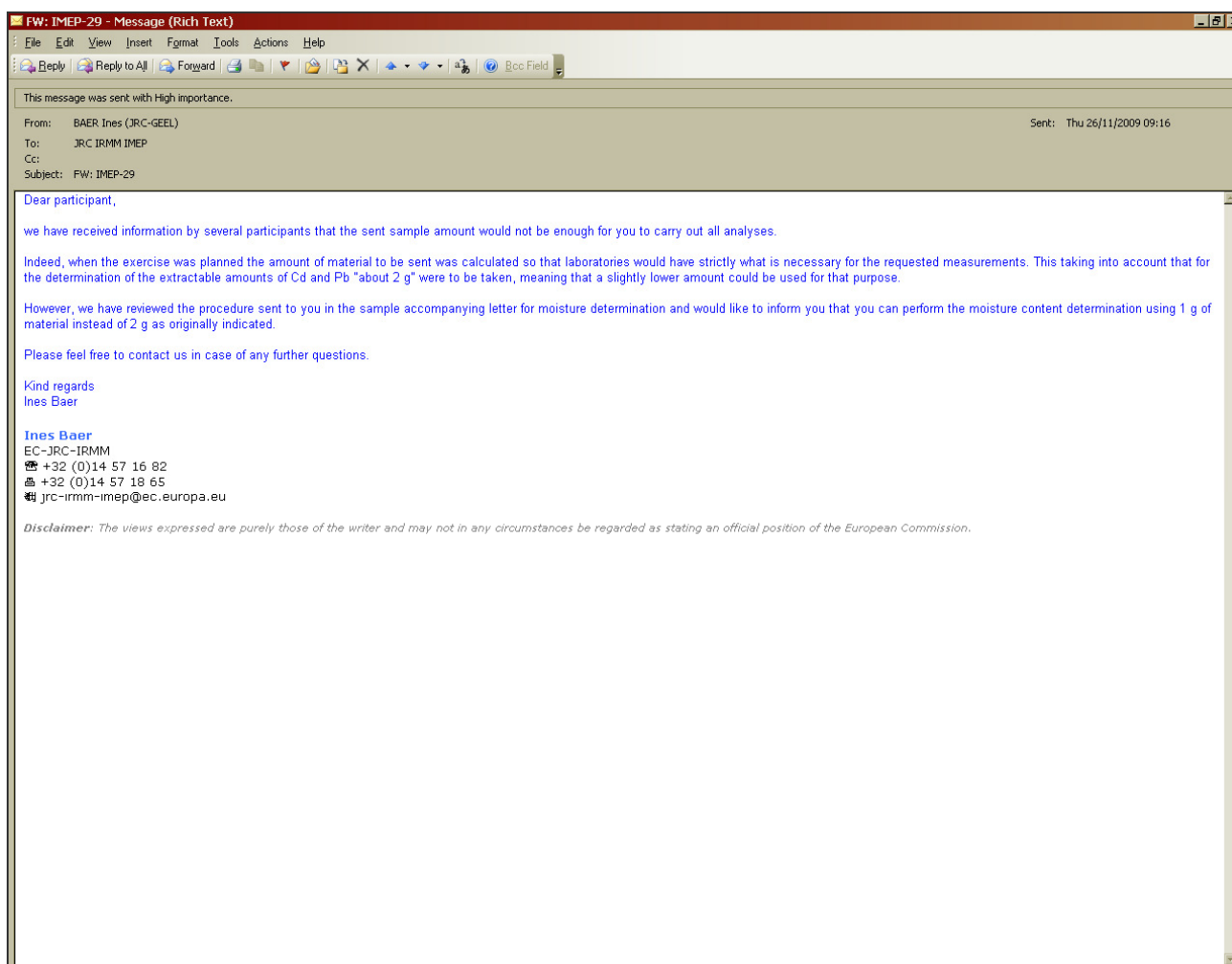
IMEP-29: Total As, Cd, Pb, Hg and Sn, and extractable Cd and Pb in feed of plant origin

Part Nr	Official Method?	If Yes, which:	If no - sample pre-treatment?	If no - digestion step ?	If no - extraction / separation step ?	If no - instrument calibration ?
3102	yes					
3198	yes			Ashing		
3229	yes	VDLUFA				
3334	no	External calibration	No pre-treatment	8 ml on Nitric Acid+2 ml of hydrogen peroxide+ Microwave assisted digestion	No	Yes
3835	yes	VDLUFA				
4041						
4148	yes	VDLUFA				
4198	yes					
4235	yes	prEN15763				
4418	yes					
5007	yes	VDLUFA MB VII, methods 2.2.29 (Hg), 2.2.2.10 (As), 2.2.2.5 (Cd, Pb)				
5041	yes	EN 13805				
5048	yes	SR EN 14082:2003				
5078	no		None	Microwave Digestion	None	External plus Internal standards for ICP-MS
5086	yes	BDS 11374				
5944	no		See no. 1.3. The shortage of material forced us to use a different kind of digestion and to quit As-determination; we do not analyse Sn in that kind of matrix.	For total element extraction we used digestion with aqua regia (1 h at 165 °C).		Routine instrument settings for measurement of Pb, Cd and Hg were used.
6024	no		no	dry ashing	no	yes
6330	no		homogenisation, sample weight: As, Cd, Pb-0.5g; Hg sample weight: ~100mg. Mercury analyser AMA 254 is a single purpose atomic absorption spectrophotometer designed for the direct mercury determination without a need of sample chemical pre-treatment. AMA 254 uses mercury vapor generation technique	As, Cd, Pb-total digestion using microwave using azotic acid, for As mixture of azotic and hydrochloric acid		calibration curves: As:0,1-10ppb; Pb:2-20ppb; Cd:0,5-3,0ppb; Hg: 1st range: 0.5-40ng, 2nd range: 40-600ng
6660	yes	§ 64 of the German Food and Feed Code (LFGB)				
6723	yes					
6736	no		maceration in concentrated nitric acid for 2 hours	microwave digestion in concentrated nitric acid (200 C, ramp time 15 min, hold time 15 min) in teflon liners	filtration of solution after digestion through separatory funnel	calibration curve method was used (CPI -International standard solutions were applied)
6814	no					

IMEP-29: Total As, Cd, Pb, Hg and Sn, and extractable Cd and Pb in feed of plant origin

Part Nr	Official Method?	If Yes, which:	If no - sample pre-treatment?	If no - digestion step ?	If no - extraction / separation step ?	If no - instrument calibration ?
6835	yes	NMKL No 186 2007, EN 13805				
6852	no			Microwave Digestion with H ₂ O and HNO ₃		
6959	no			Acid digestion(HNO ₃) + microwave system		five calibration levels
7022	yes	NF EN 15510:2007				
7027	yes	SR EN 14082:2003; SR6182-22:1995				
7214	yes					
7357	no		wet digestion, concentrated nitric acid	about 40-50 degrees over night, gradually to 120 degrees (5 hours)		
7669	yes	Microwave digestion by ICP-MS				
7813	yes	Pb- EPA M 239.2, Cd- EPA M 213.2, As- EPA M 206.2, Hg- EPA M 245.1				
7985	no		about 0.2g of samle into a microwave Teflon boat, HNO ₃ and H ₂ O ₂ were added	250W 2min, 0W 2min, 250W 5min, 450W 5min, 650W 10min		standard curve calibration
8211	no		none	Nitric acid digestion in microwave	?	Standard addition method/external standard calibration
8442	no			10 ml ac nitric 65%/g , Closed -vessel microwave 5 steps max 180°C.		Standard solutions of 5 concentration levels.
8917	no		none	0.5 g sample in 5 ml nitric acid using microwave heating and cealed quartz vessel	none	External standards plus internal standard correction
9034	no		None	Microwave digestion (nitric acid 65% + peroxide hydrogen 33%)	None	Standard addition method
9291	yes					
9568	yes	methods publishes by § 64 LFGB (Germany)				
9611	yes					
9763	yes	AOAC				

Annex 19 : Email sent to participants during exercise



European Commission

EUR 24318 EN – Joint Research Centre – Institute for Reference Materials and Measurements

Title: Total arsenic, cadmium, lead, mercury and tin, and extractable cadmium and lead in feed of plant origin

Author(s): Ines Baer, Agnieszka Krata, Christophe Quétel, Inge Verbist, Thomas Linsinger, Elżbieta Perez Przyk, Beatriz de la Calle

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Abstract

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme IMEP. It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of total As, Cd, Pb, Hg and Sn, and extractable Cd and Pb in feed of plant origin following Directive 2002/32/EC of the European Parliament and of the Council on undesirable substances in animal feed.

The test material used in this exercise was a candidate reference material, the matrix being rye grass. The material was relabelled and dispatched to the participants in the second half of October 2009. Each participant received one bottle containing approximately 10 g of test material. Sixty-two participants from 23 countries registered to the exercise of which 59 reported results.

The assigned values (X_{ref}) for total Cd, Pb, As, Hg and Sn were the reference values as obtained during the certification campaign taking place simultaneously to the ILC. The assigned values for extractable Cd and Pb were provided by IRMM using isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS).

Participants were invited to report the uncertainty of their measurements, which was done by around 90 % of them. The laboratory performance was evaluated using z- and ζ -scores in accordance with ISO 13528. The standard deviation for proficiency assessment (also called target standard deviation), $\hat{\sigma}$, was fixed at 15 % for all measurands on the basis on the outcome of previous ILCs.

The outcome of the exercise was altogether positive, with 68 % or more of the participants reaching satisfactory z-scores for all measurands except for total As and Hg, which appeared to be problematic in this exercise, showing a non-normal results distribution and tendency to very high means. The ζ -scores were not as good as the z-scores, which indicates a persisting problem of appropriate uncertainty estimation. Finally, total Sn was included for the first time in an ILC. Results were better than expected, but can certainly be improved.

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